Femtosecond Laser ablation/ICPMS for trace element and isotope ratio measurement: application to biomineral, petroleum industry and forensic science... And poetry!

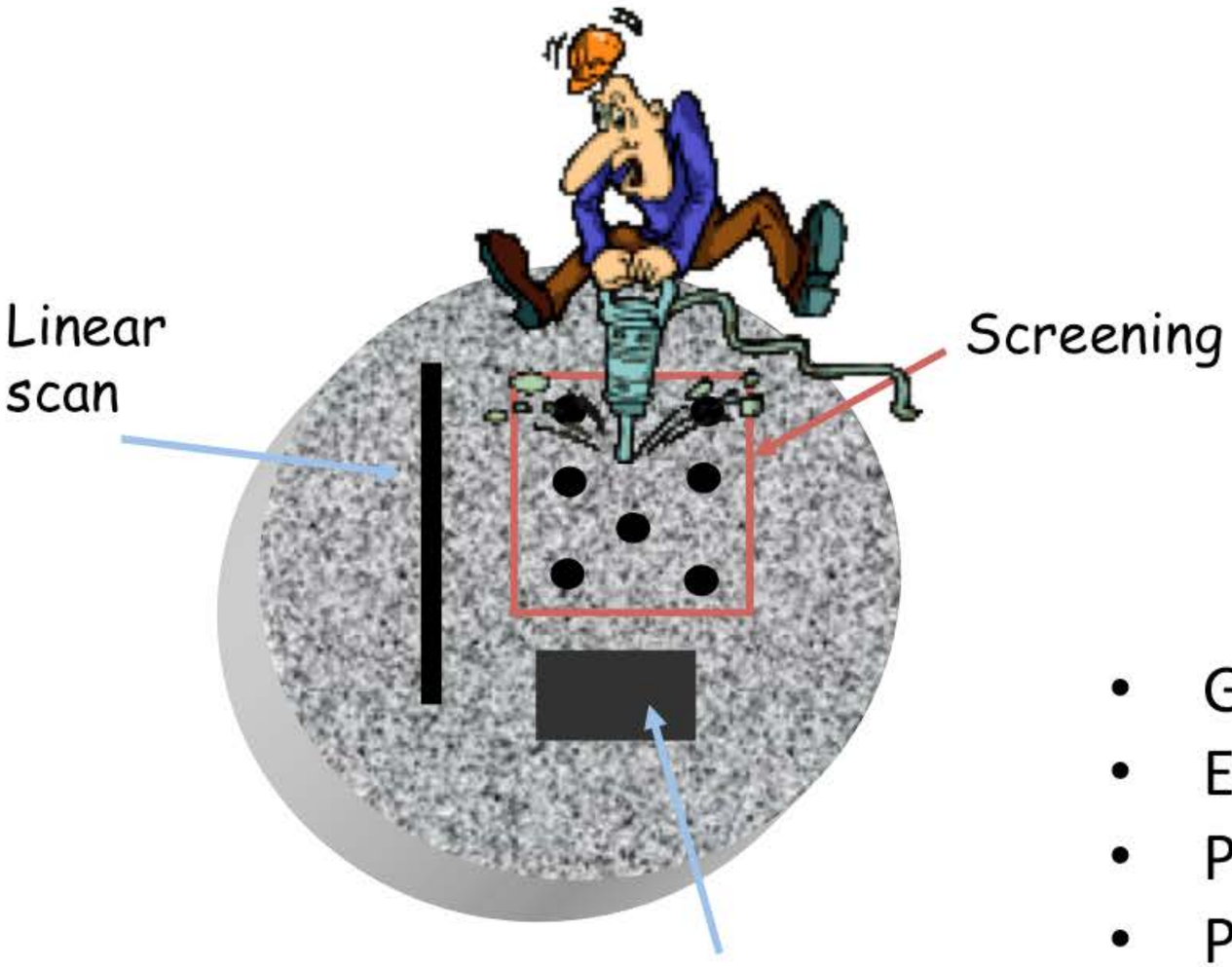
Christophe Pécheyran

Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE),
UMR CNRS-UPPA 5254 IPREM, Hélioparc Pau Pyrénées, 64053 Pau, France

christophe.pecheyran@univ-pau.fr

Laser ablation for direct solid sampling

Direct analysis
Micro sampling (5-200 µm)
Macro sampling (>200 µm)
Minimizing invasive approach

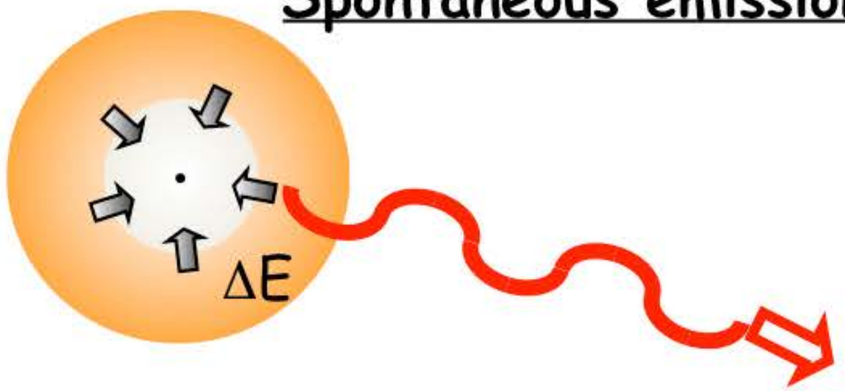



Depth profiling

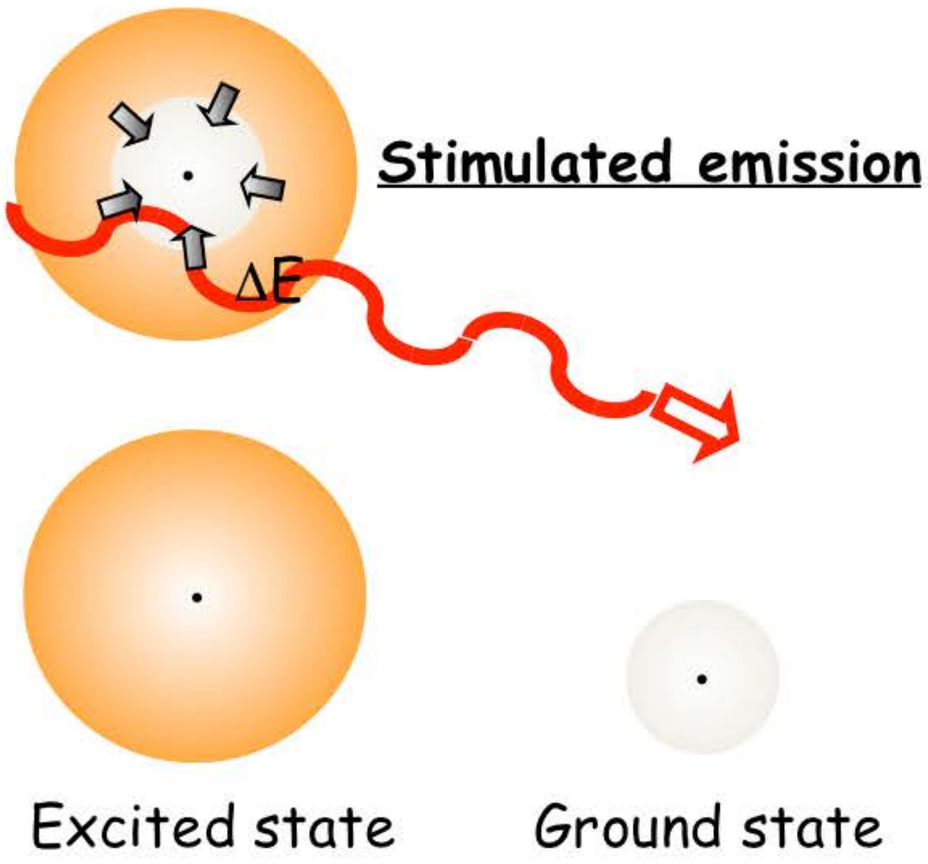
- Geosciences
- Environment
- Protéomic
- Petrochimistry
- Forensic
- Archeology
- Surface analysis...

Laser basic principle

Spontaneous emission

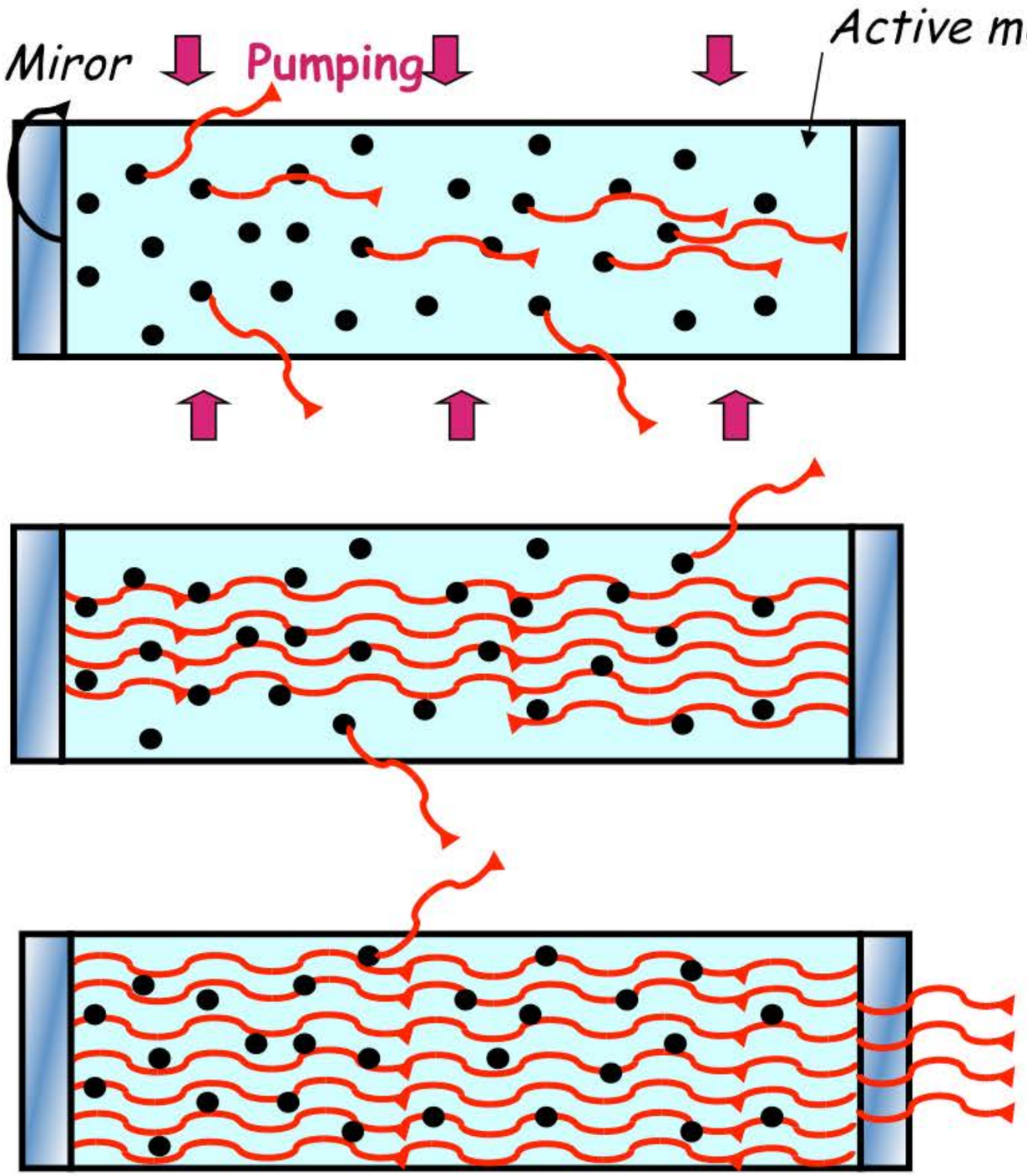


Spontaneous emission: the energy accumulated by an atom is released via the emission of a photon.



Stimulated emission (discovered by A. Eintein) : induced by a photon on a excited atom, this phenomenon leads to the emission of a photon of the same energy, same direction and phase (**coherent light**).
When a population inversion is present the rate of stimulated emission exceeds that of absorption, and a net optical amplification can be achieved
This property is used to generate laser light...

Laser basic principle



Resonator

The population inversion is triggered by an external source of energy (pumping: light flash, electric source, or even lasers)

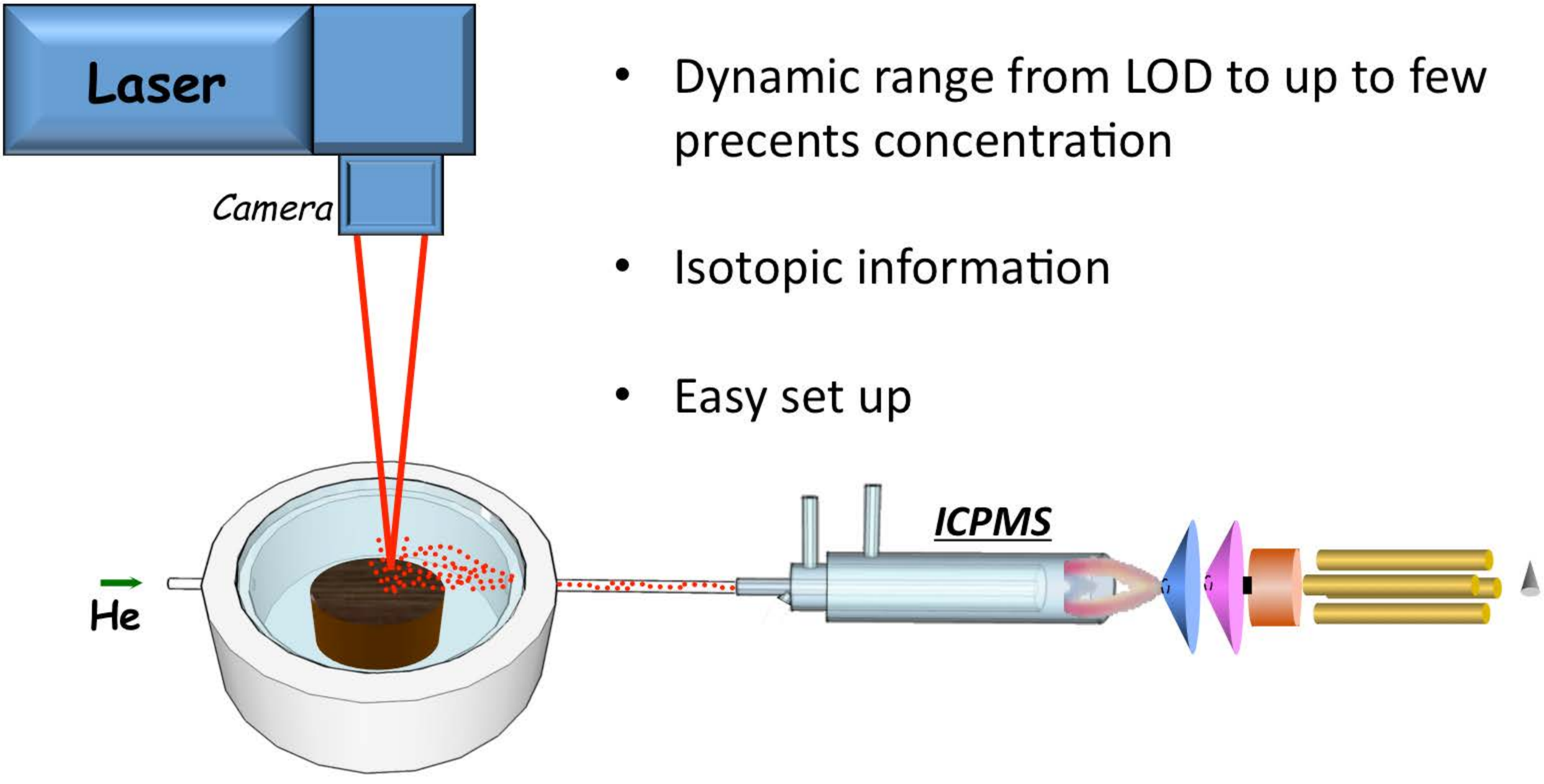
Combined with a resonator (2 mirors and an active medium), the laser light can be accumulated in the axis of the resonator.

The active medium might be a crystal, a gas, or a liquid.

When the accumulated energy is high enough, and before destroying the resonator the end mirror is made transparent to the light (using a Pockels cell)

Laser ablation-ICPMS

- Limits of Detection from sub ppb to ppb range
- Dynamic range from LOD to up to few precents concentration
- Isotopic information
- Easy set up



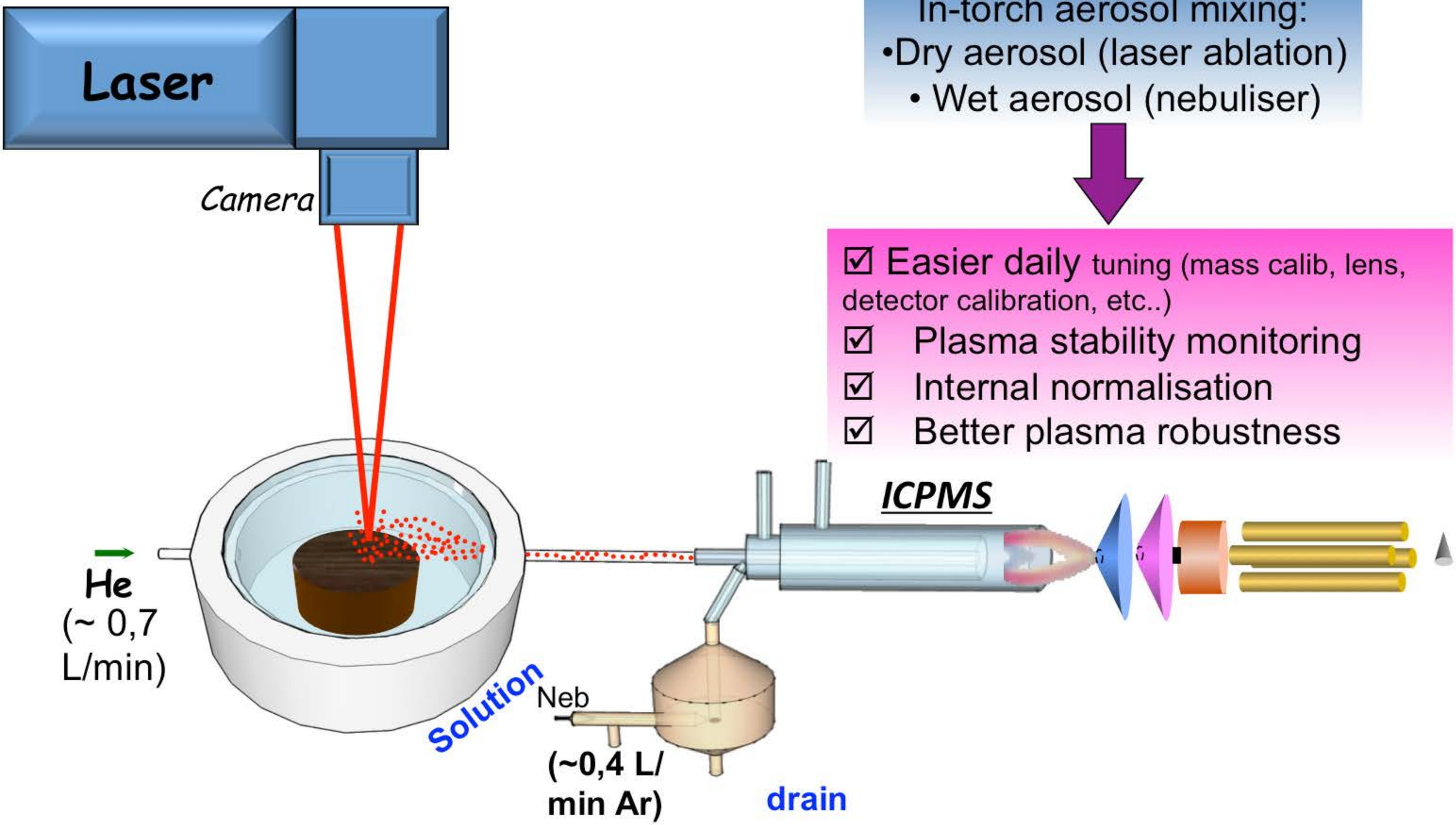
Laser ablation-ICPMS set up

Wet versus Dry plasma:

In some conditions (i.e when the oxydes level is not a problem), the LA/ICPMS coupling can be used in wet plasma configuration with some advantages:

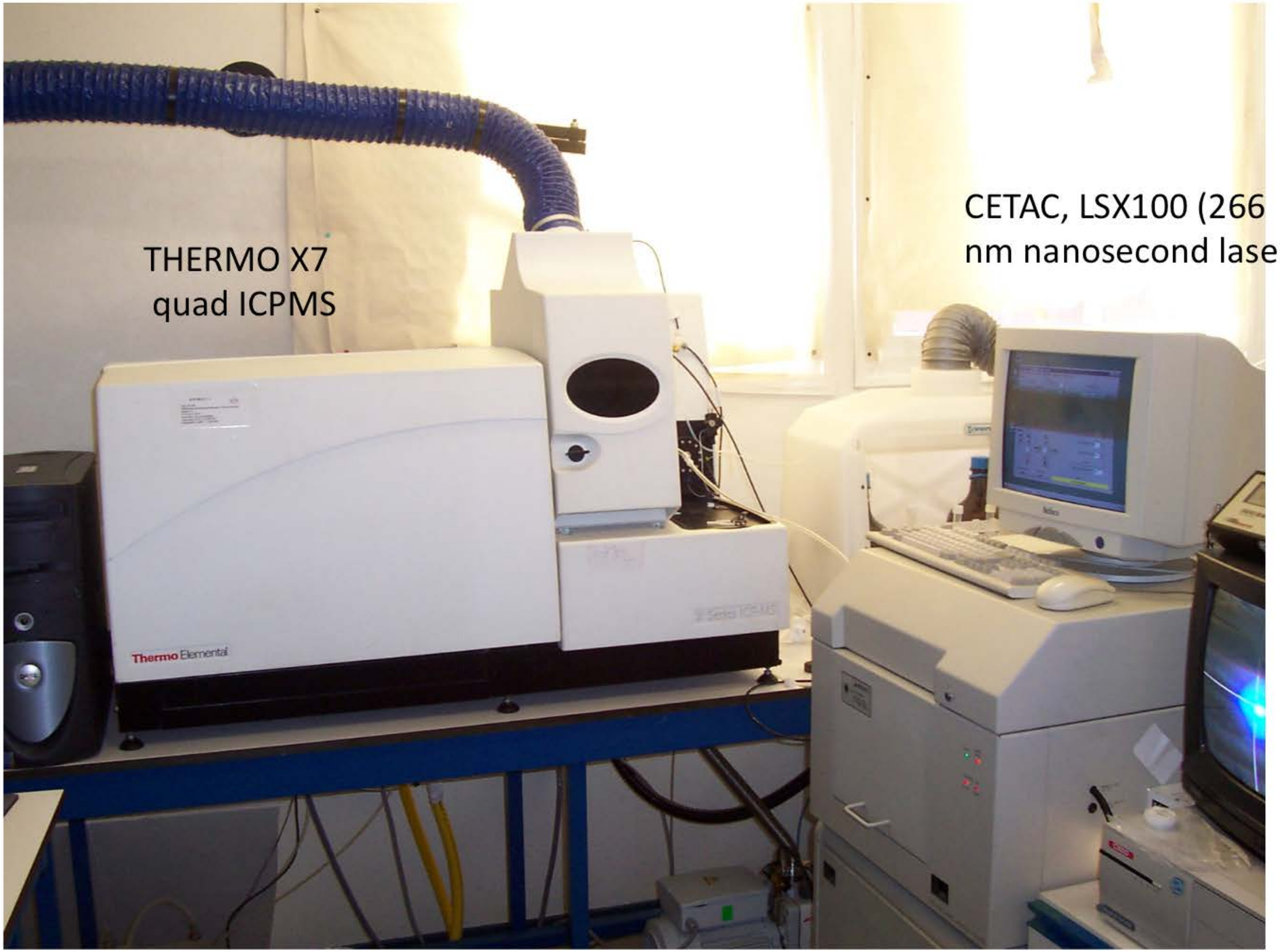
In-torch aerosol mixing:
- Dry aerosol (laser ablation)
- Wet aerosol (nebuliser)

☑ Easier daily tuning (mass calib, lens, detector calibration, etc..)
☑ Plasma stability monitoring
☑ Internal normalisation
☑ Better plasma robustness



The ICPMS family...

Laser ablation-ICPMS set up

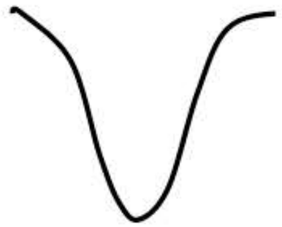


Various laser types...

Type	Longueur d'onde	Energie/ impulsion	Longueur d'une impulsion	Diamètre faisceau primaire	Fréquence de tir
	nm	J	ns	mm	Hz
CO2	10600	0.3	100-1000	2-5	100-1000
Rubis	694	1	10-100	10-25	0.1
Nd :YAG fondamental	1064	0.5	~ 4 - 100	5-10	1-20
Nd :YAG harmonique 4	**266**	0.003-0.009	"	"	"
Nd :YAG harmonique 5	**213**	> 0.001	"	"	"
KrF	248	0.002	10-100	20x10	1-100
ArF	**193**	0. 2	10-100	20x10	1-100
Femtoseconde	196-265-800-257 – 515- 1030	0.0005	0.0001 – 0.0004	4	1-10000

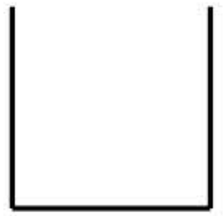
- UV nanosecond lasers (266, 213 and 193 nm) are the most used in analytical chemistry.
- Femtosecond lasers, more expansive, though having better performance are less used.

Some definitions



Gaussian shape

Gaussian shape: the beam energy distribution of a laser is naturally gaussian: when drilling a hole, the resulting crater shape is gaussian (or conical in a first approximation)



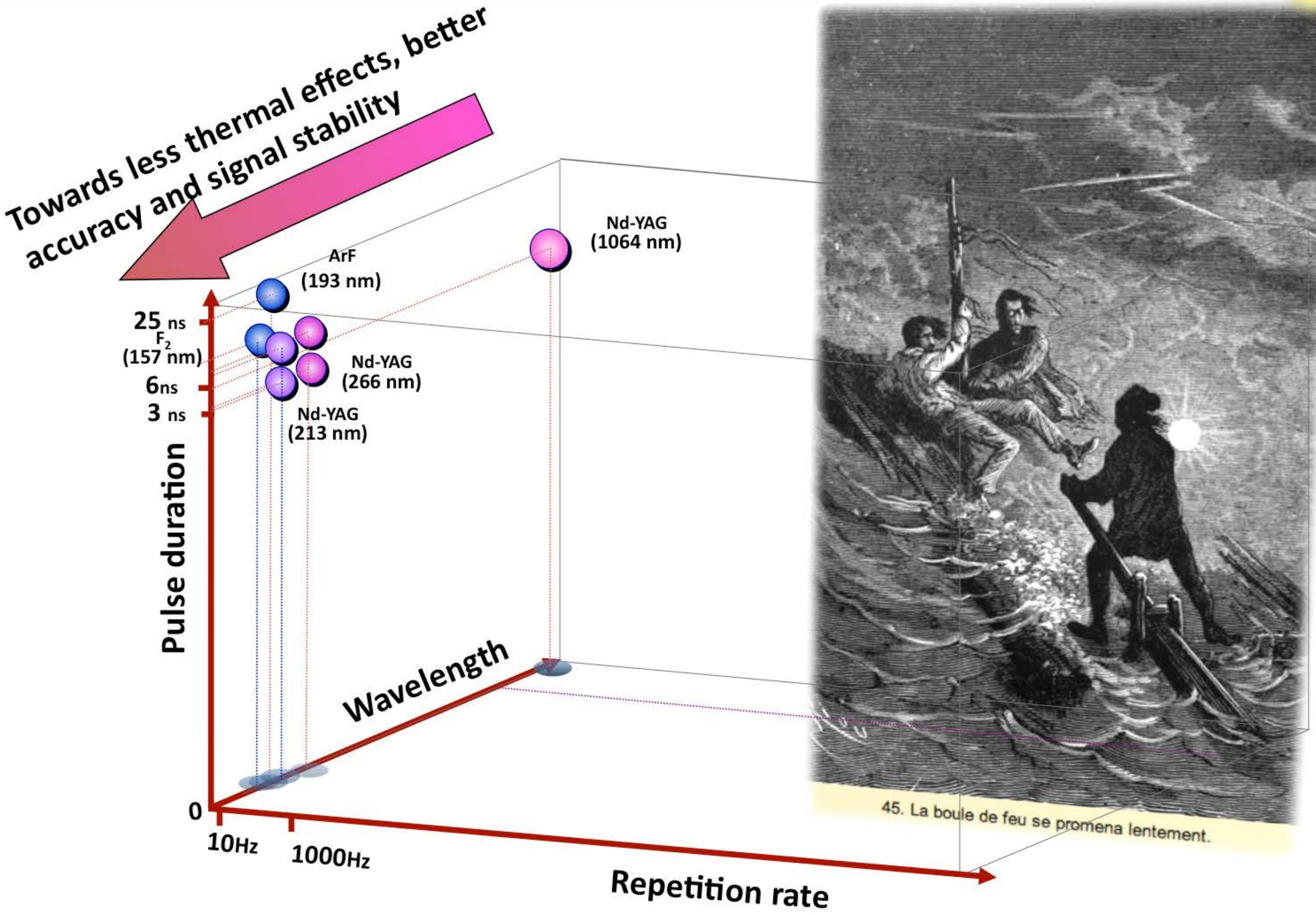
Flat top

Flat Top : some optical arrangements allow homogenising the energy profile : the resulting crater is now a cylinder.

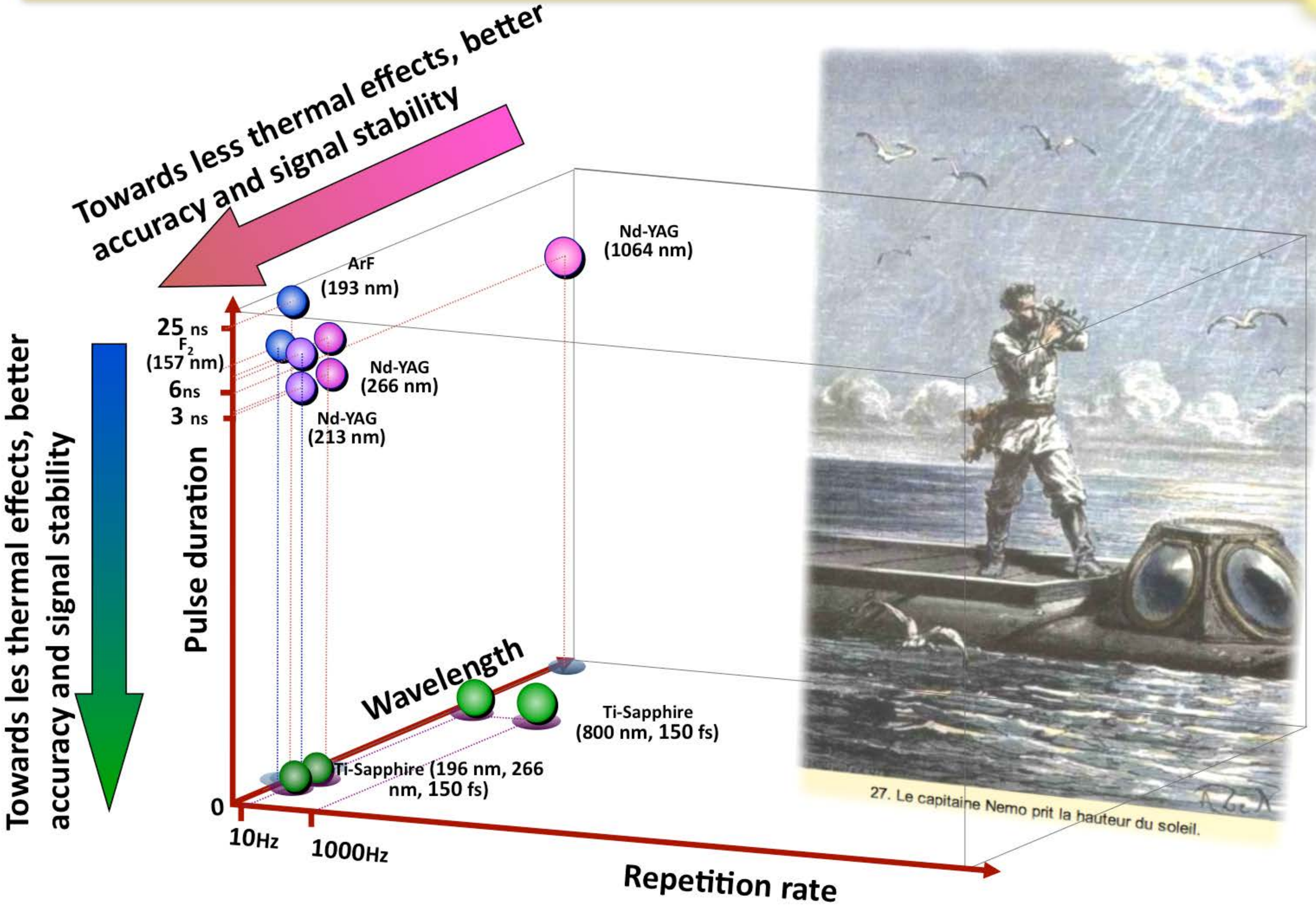
Fluence (J/cm²) : energy per pulse/ laser beam size at the surface of the sample.

Power density (W/cm²) : Fluence/pulse duration

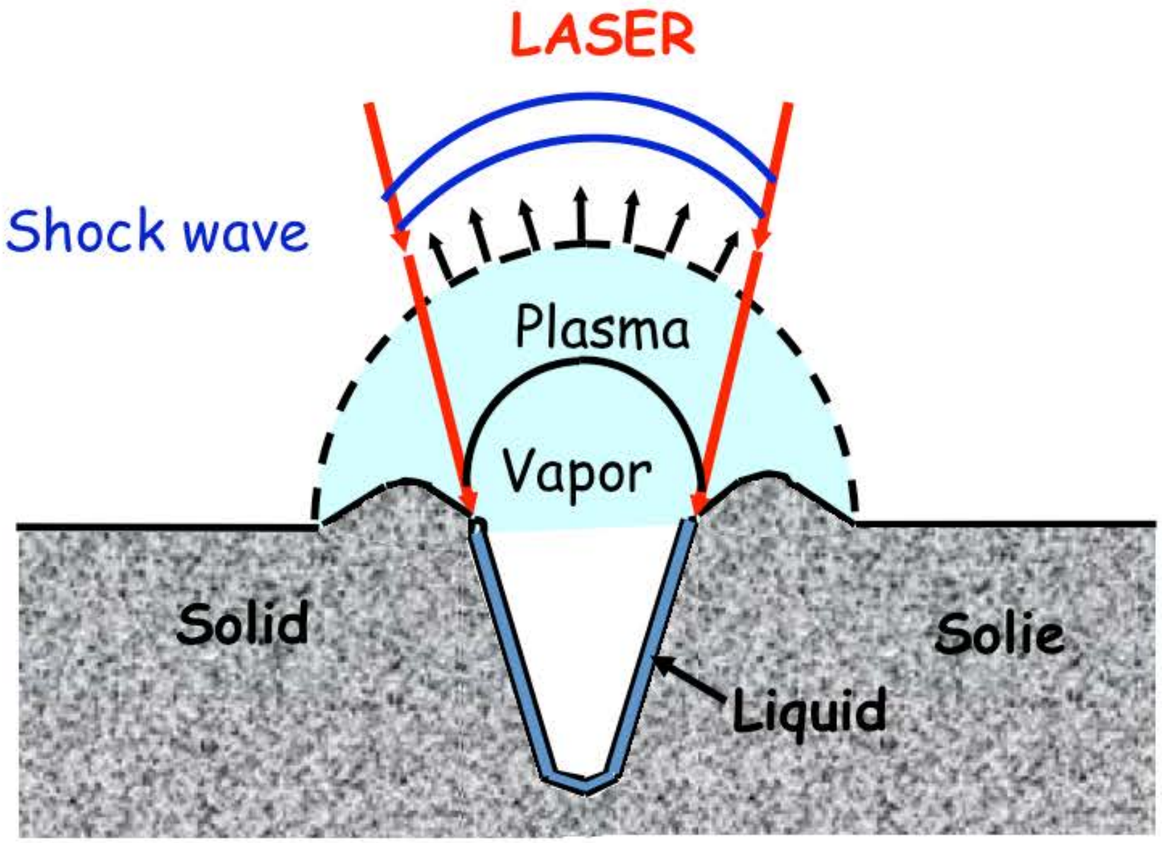
LA/ICPMS since 1985 in 3D…



Advances in LA/ICPMS since 2003 in 3D



Ablation processes



3 main processes take place during the ablation:

- **1st step**: the laser energy is absorbed, converted into heat. when the heat is not dissipated then melting and sublimation can occur. This occurs at low power density (<10^6W/cm^2). In contrast, when the power density is high enough (>10^9W/cm^2), ie high energy or/and short pulse duration, "spontaneous" sublimation occurs that will generate **explosion and ejection of particles by fragmentation**.

- **2d step**: free electron occuring in the vapor phase and those formed by thermal isonisation lead to the formation of a micro plasma at the surface of the sample.

- **3rd step**: the plasma expands and generate a shock wave.

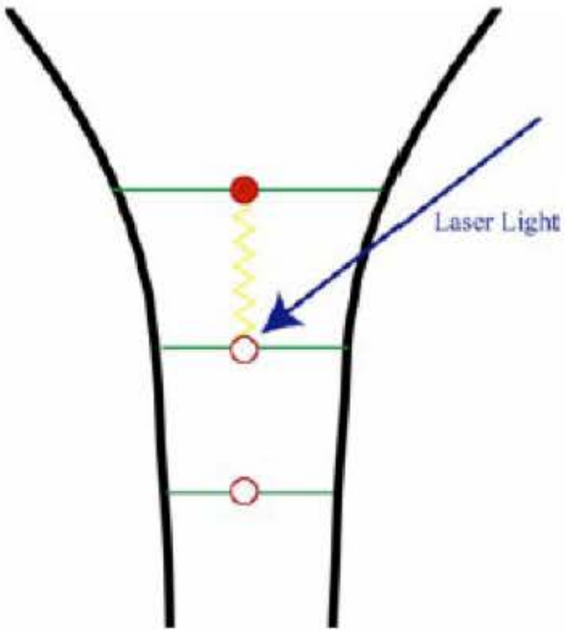
laser ablation time scale

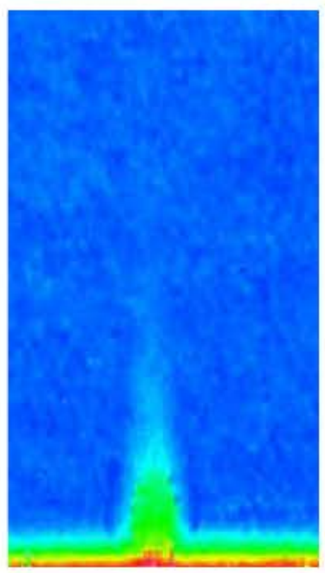
Electrons absorb photons
Femtoseconds

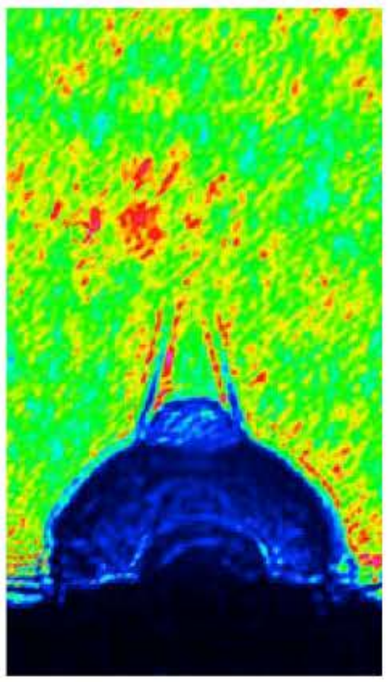
Electron emission from the surface
Picoseconds

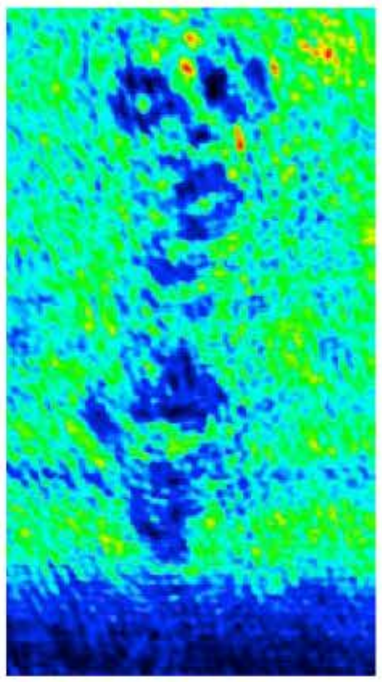
Plasma formation
Nanoseconds

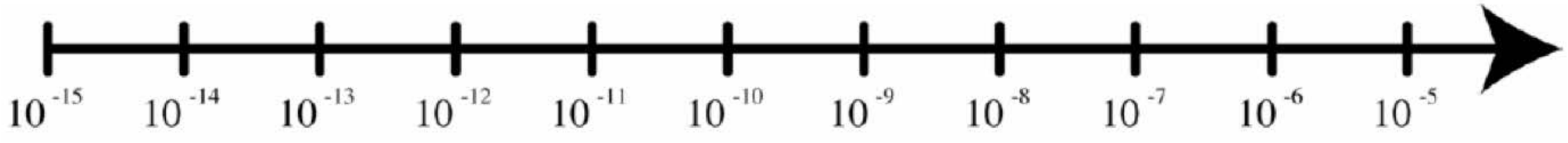
Particles ejection
Microseconds











Time(seconds)

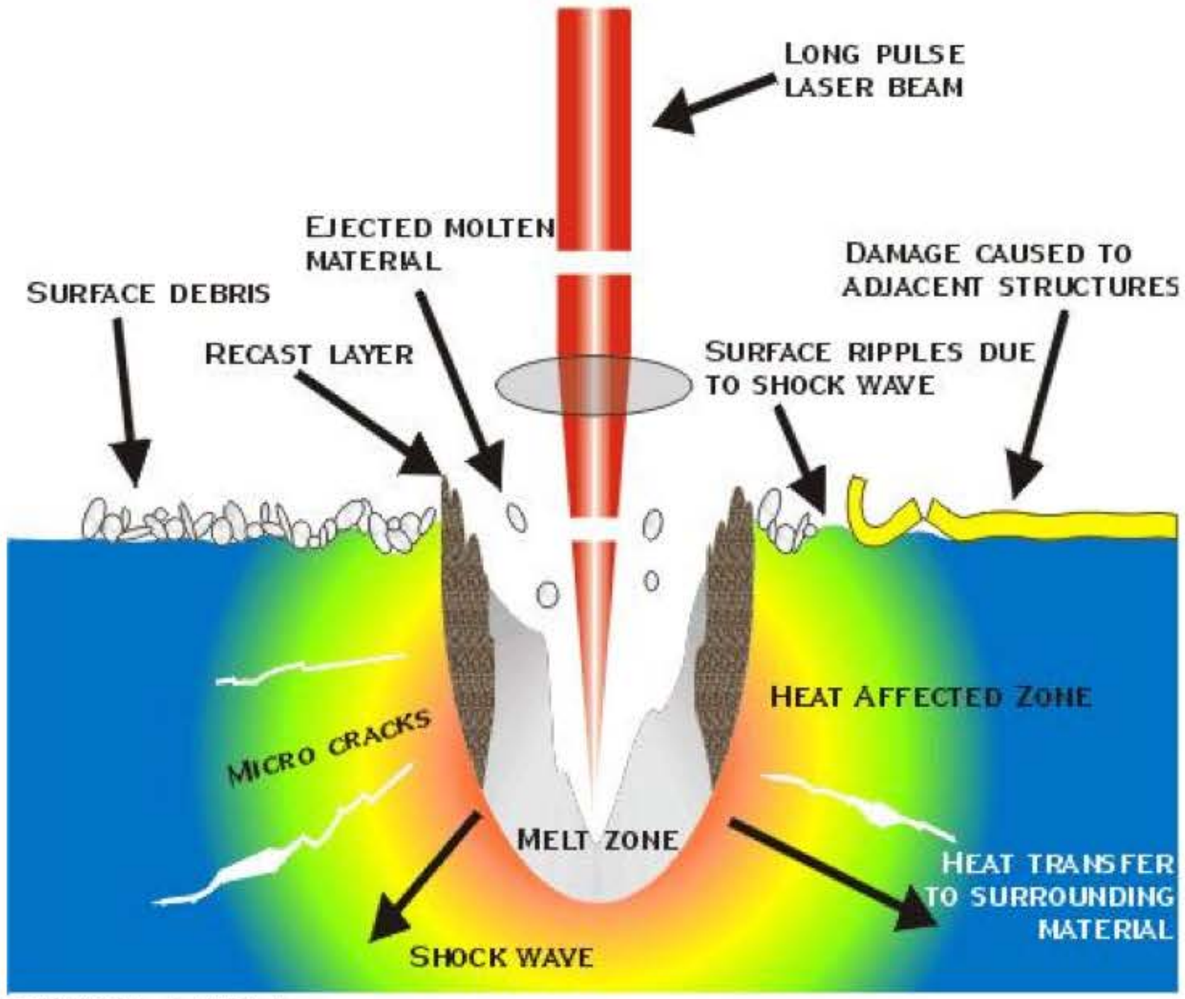
Adapted from R. Russo – Winter conférence 2004

Short pulse *versus* Ultra Short pulse

Short pulse

few **nanoseconds**

(10^{-9} s)



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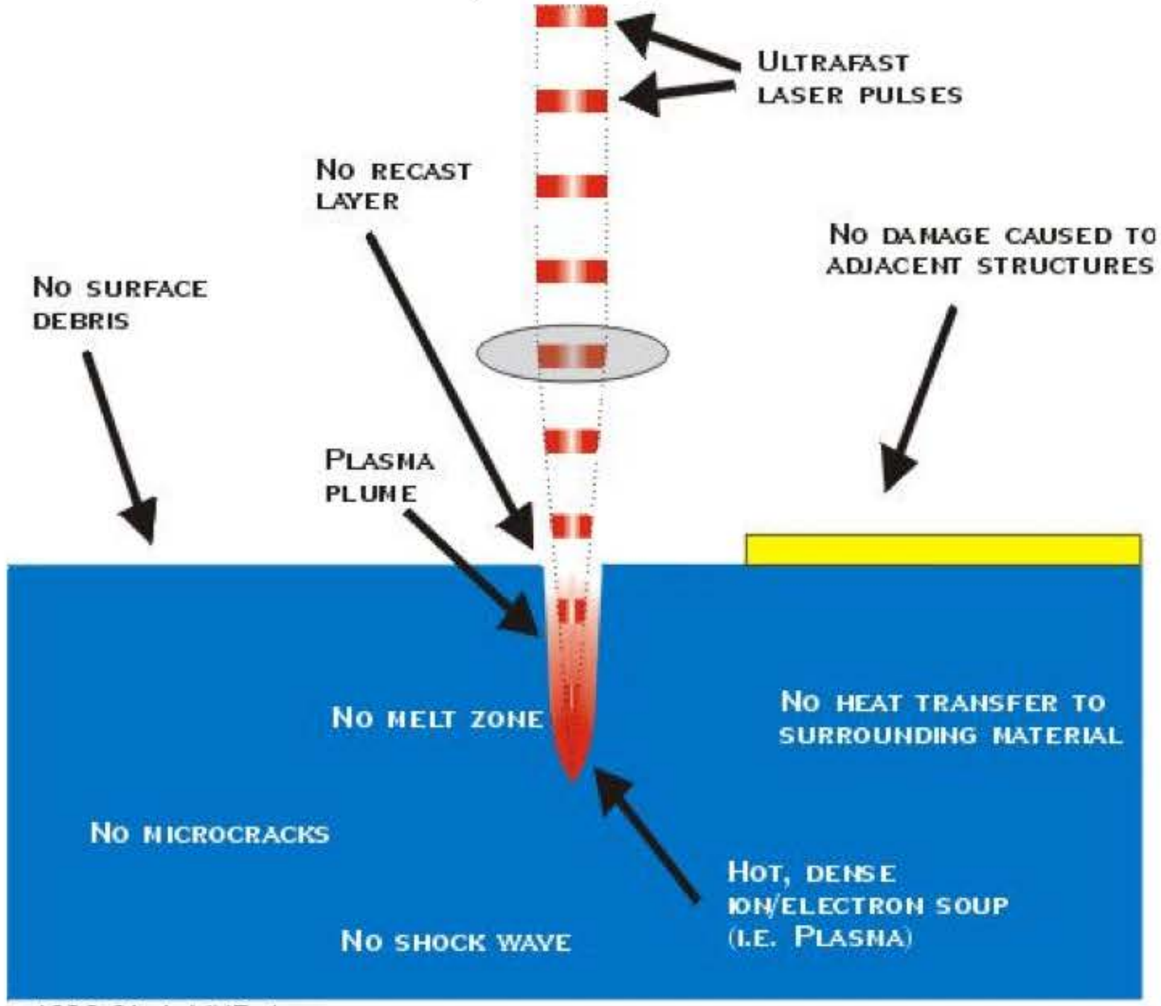
Ultra short pulse

hundreds **femtosecondes**

(10^{-15} s)



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Thermal effects

⇒ **accuracy**

=> **in-depth resolution**

Very limited thermal effects

⇒ **better accuracy** (due to small particles)

⇒ **better in-depth resolution**

Ablation processes

At low power density (10^6 W/cm^2), the vaporisation is the dominant process and the ablated material is made of vapor, aerosol, melted particles. These conditions should be avoid as much as possible (see below).

Beyond 10^9 W/cm^2, the process becomes explosive and thermal effects are reduced.

In addition, the micro plasma formation can interact with the sample and generate additional melting and vaporisation.

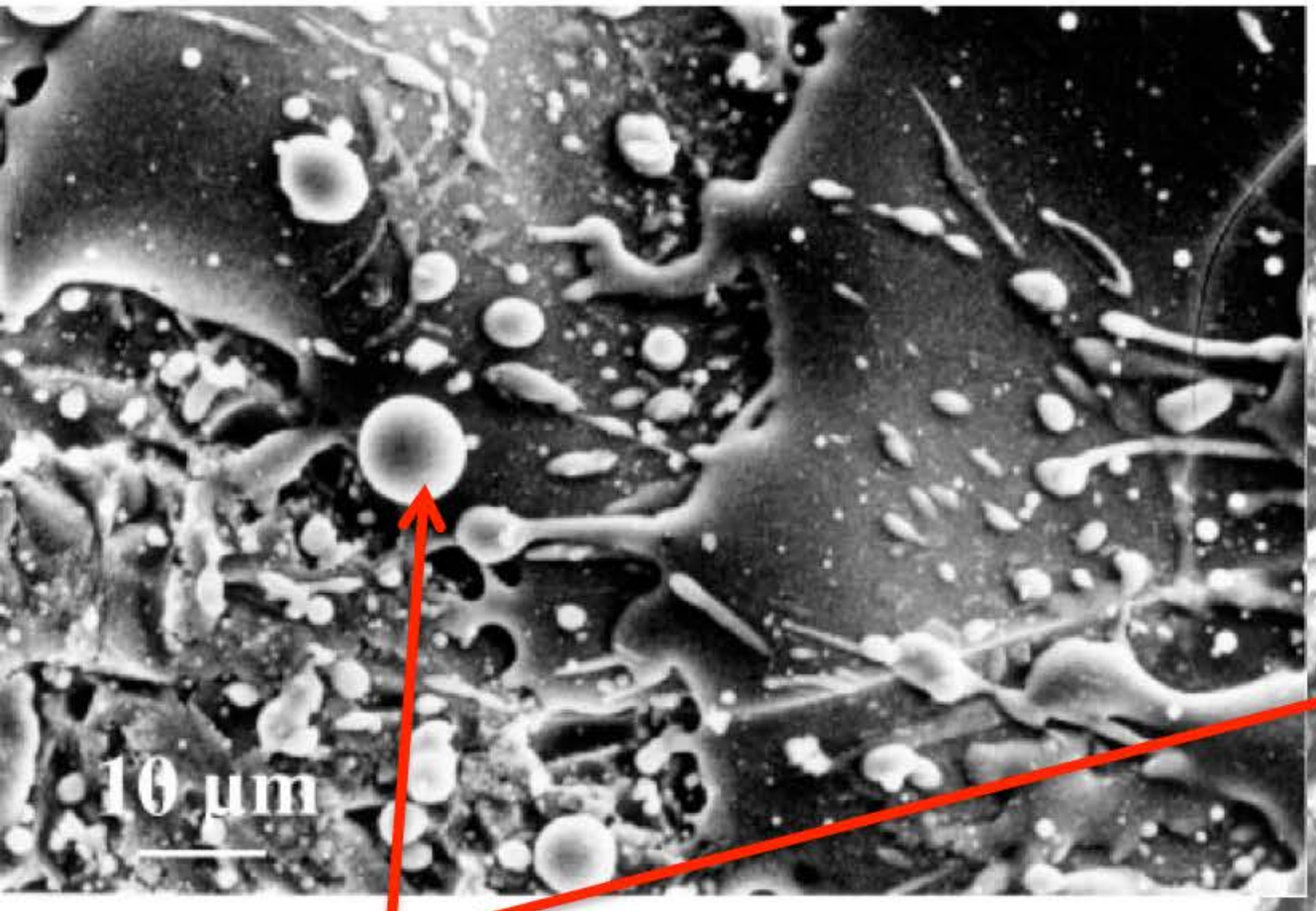
The interaction between the laser light and the sample is a dynamic process governed by the laser properties AND the sample characteristics :

LASER	
Laser source	Wavelength, energy, pulse duration, repetition rate
laser beam	Size, focus
SAMPLE	
Optical	absorption, reflectance
Thermal	conductivity, specific heat of vaporisation
Mechanic	

Typical craters

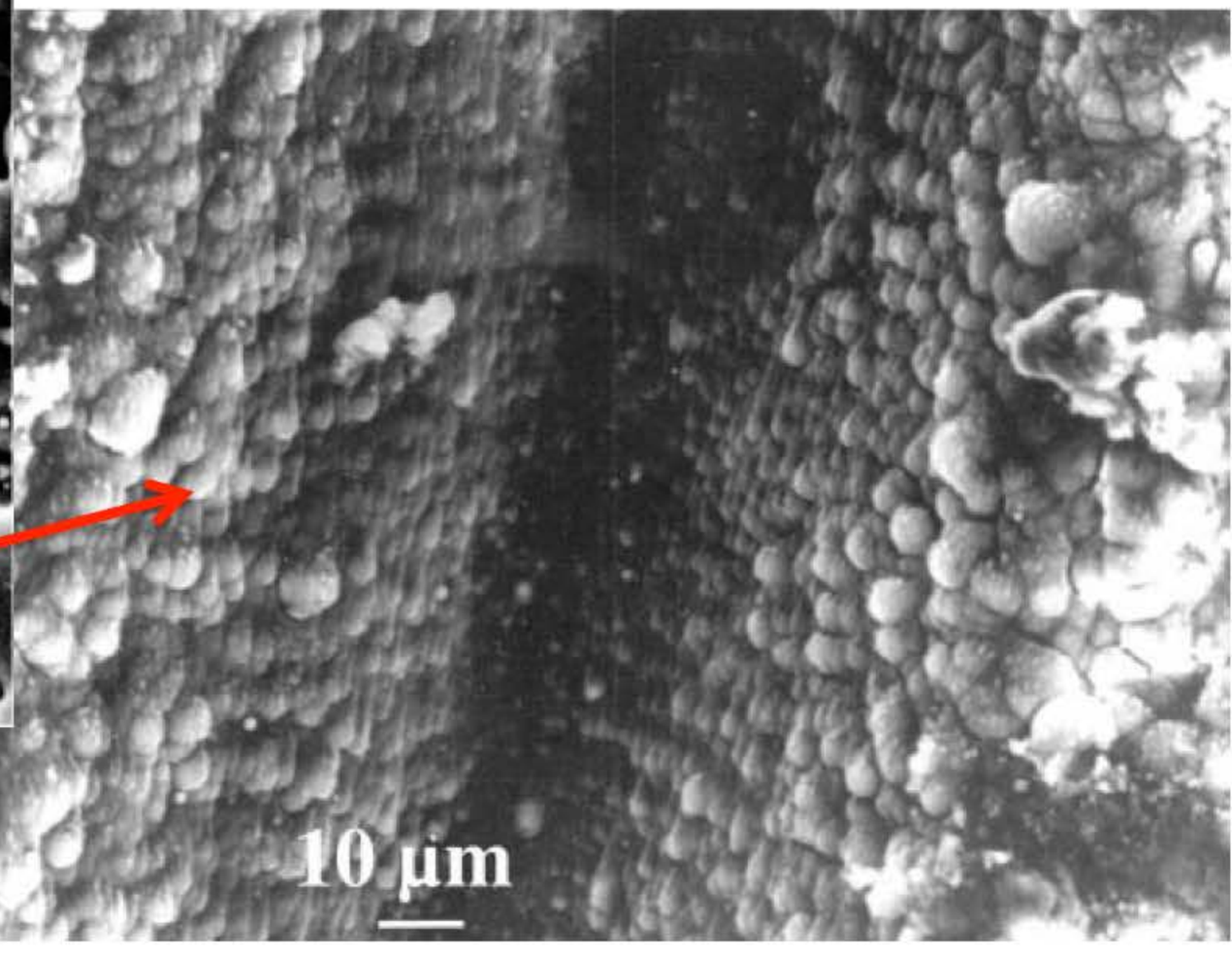
Glass samples

Nanosecond IR (1064 nm) laser:
evidence of high thermal effects (melting)



The chemical composition of the spheres might differ from the initial material composition...

Nanosecond UV (266 nm) laser. reduced thermal effects, but still there...

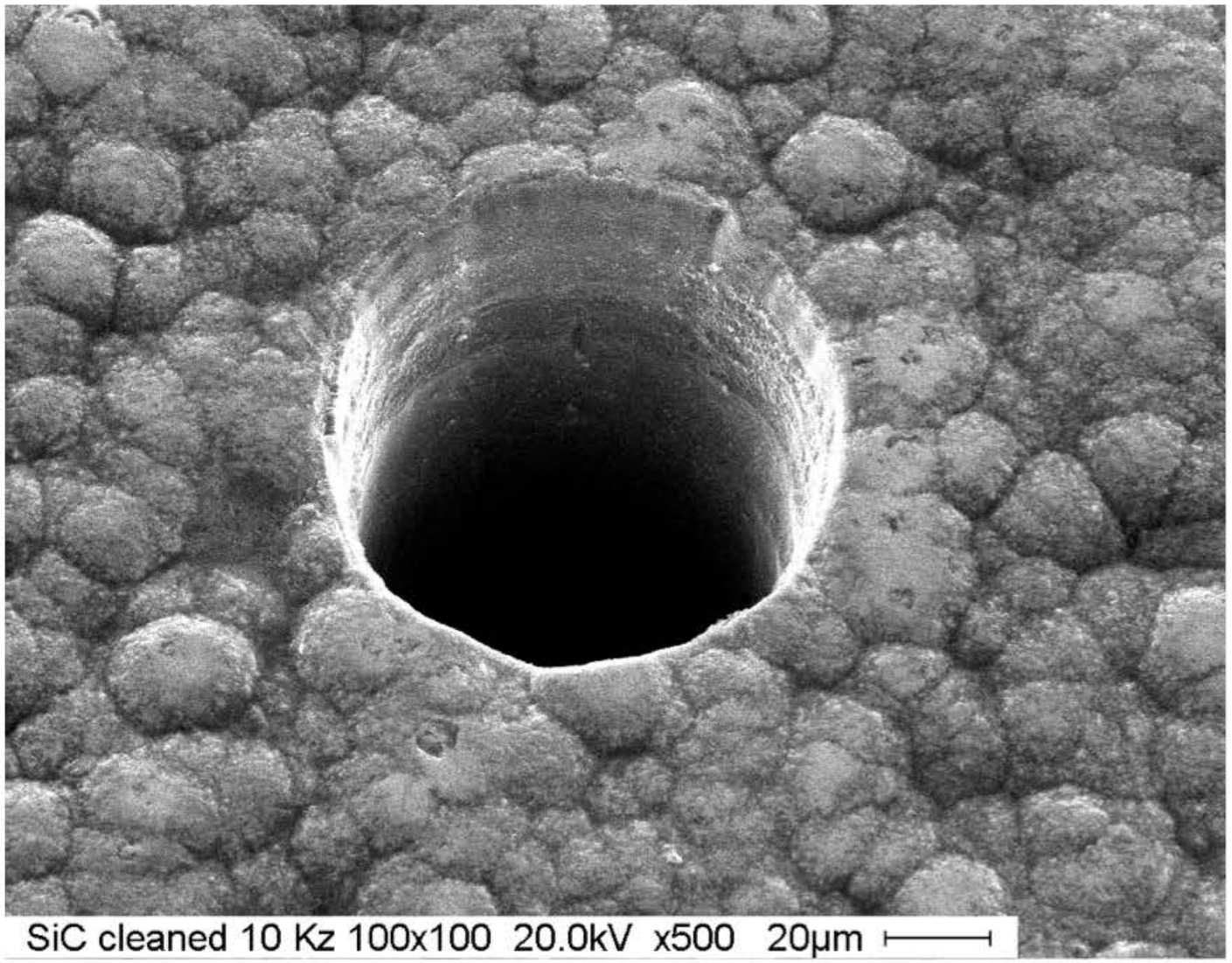


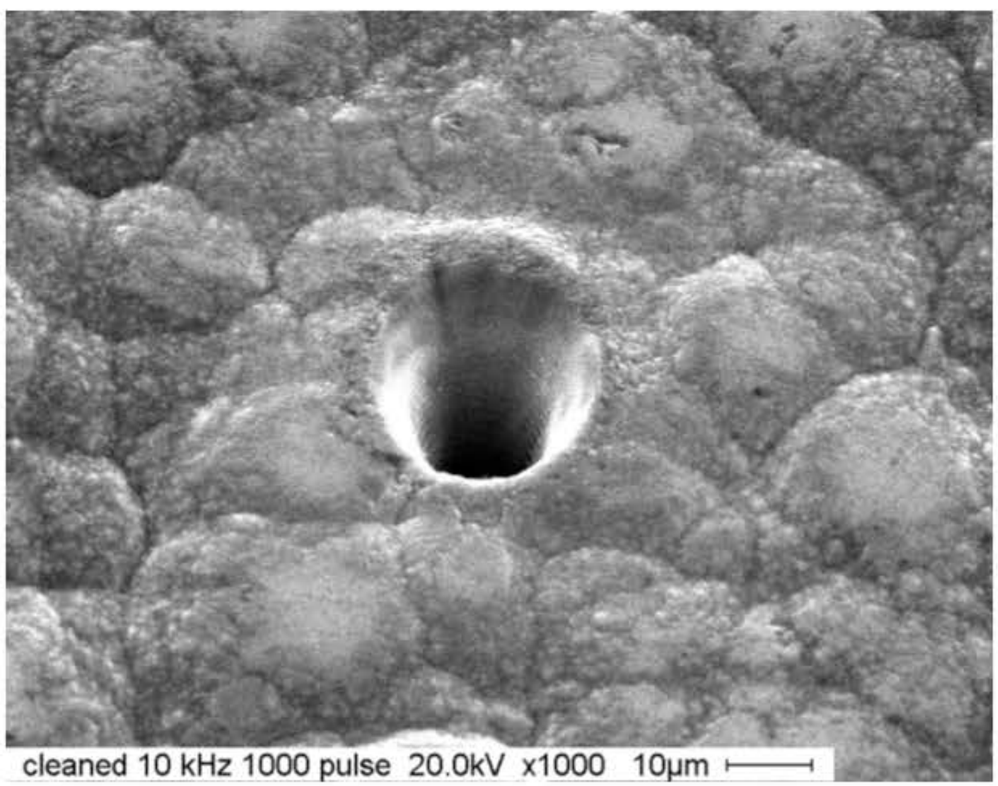
"Micro- and macro-scale investigation of fractionation and matrix effects in LA-ICP-MS at 1064 nm and 266 nm on glassy materials", M. Motelica-Heino, P. Le Coustumer, and O. F. X. Donard, *J. Anal. At. Spectrom.*, 2001, 16, 542–550

Typical craters

SiC ablated with femtosecond IR (1030 nm).

No evidence of significant thermal effects





Carrier gas

Garrier gas influence: the analytical performances are better when Ar is replaced by He : => better cooling effect (then smaller particles), and particles are more easily extracted from the bottom of the crater. The particles are however better transported in an Ar stream, that's why Ar is added post ablation cell. The sensitivity improvement is about 2-3 when using He in the ablation cell.

Ar Carrier Gas
~3.8 x 10^{-5} cal/sec °C cm

He Carrier Gas
~3.2 x 10^{-4} cal/sec °C cm

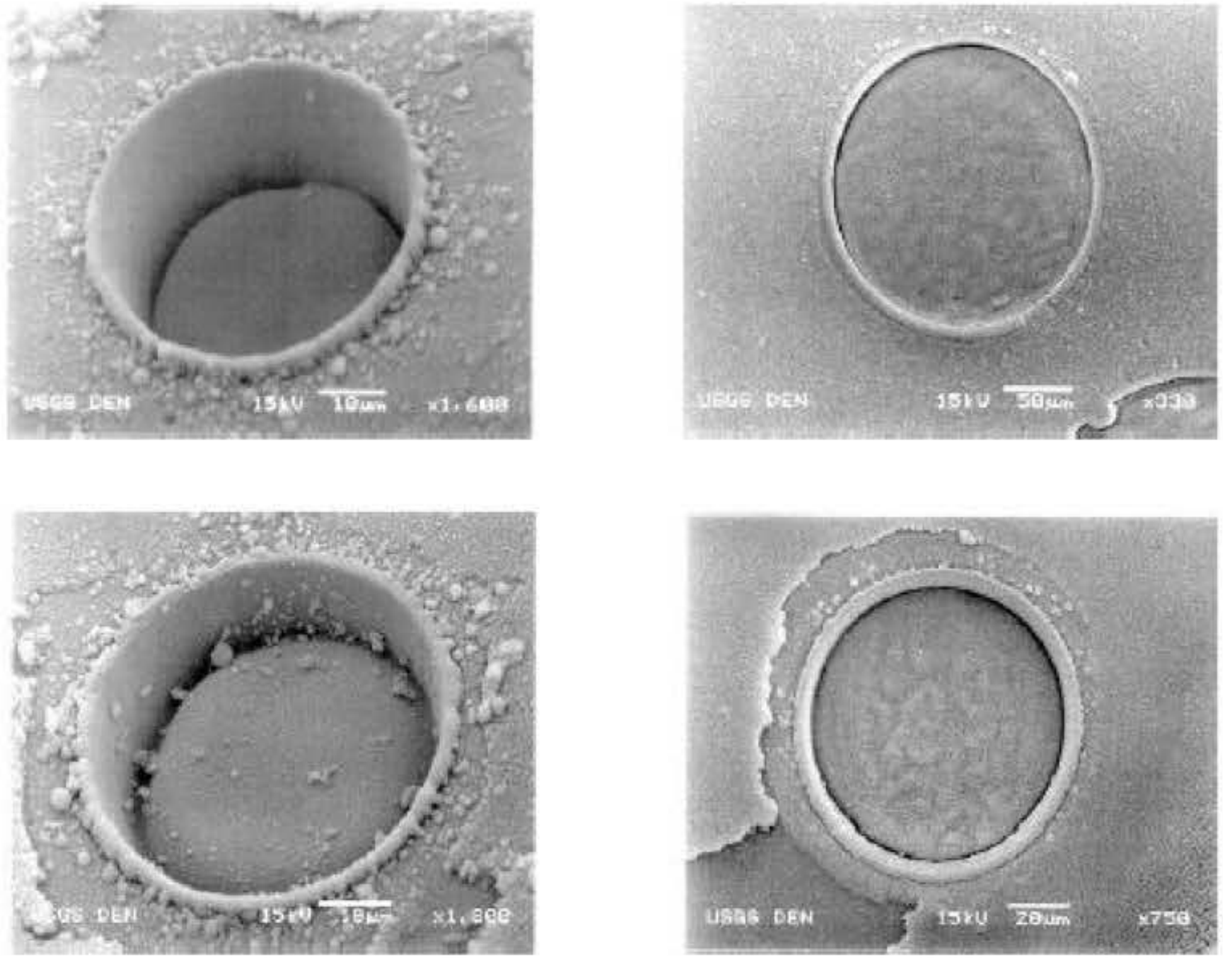
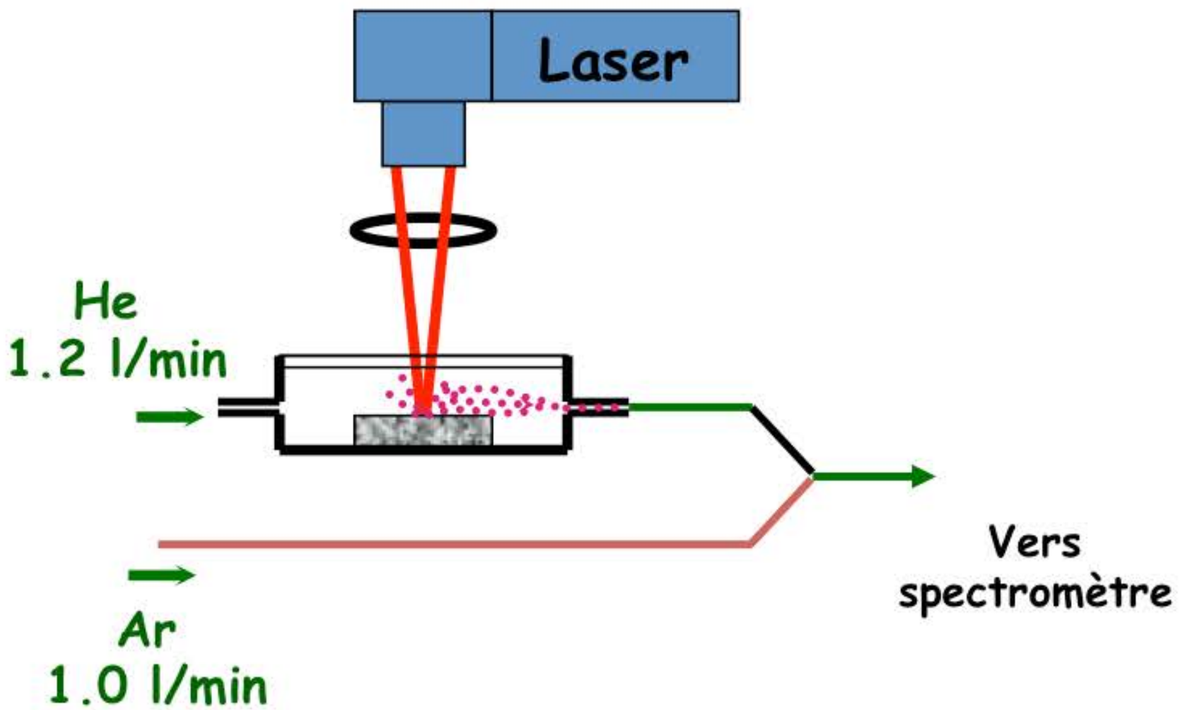


Figure 7: Gas Effects: Crater Characteristics in NIST 612 Glass (images courtesy of USGS Denver CO, USA)

Cetac LSX 200 – 266 nm

In addition, the spectral background being reduced when adding He in the ICPMS, LOD are finally improved by a factor 10 (this phenomenom is more pronounced at 193 nm compared to 266 nm).



D. Gunther et al, JAAS, 1999, 14, 1363-1368

Sample preparation

LA/ICPMS requires very limited sample preparation. However flat sample surface generally facilitates laser focussing (better visualisation).

Powders (eg: clays, sands, aerosols, sediments, etc) must be fixed:

⇒ compaction (binder addition (ex : paraffin), drying and palletisation with high pressure hydraulic press).

⇒ Lithium borate fusion ($Li_2B_4O_7$).

Small samples must be embedded into a resin

Binders and Li borate might induce contamination.

It is well indicated to pre-clean the sample surface by ablating the desired zone with low energy (close to the ablatio threshold) laser conditions; only few shots are required.

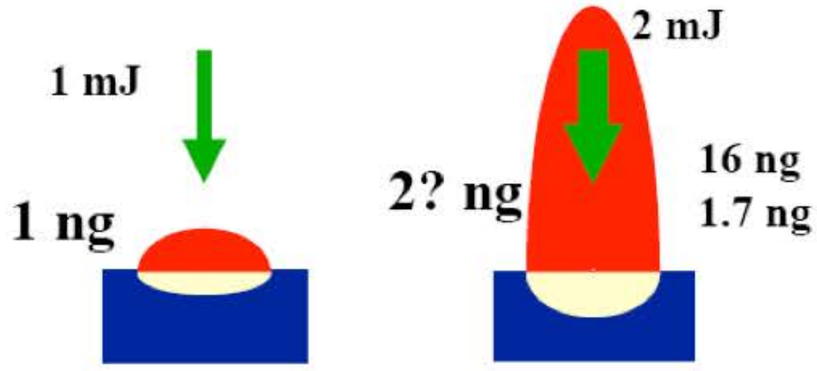
Quantification

The reason why you will need, sometimes, to spend a lot of money for high performance laser systems (from 60 k€ to >400 k€...)

Quantification

The quantification is the Achilles heel of laser ablation. Quantification is sometimes challenging because the ablation processes depends on the sample properties.

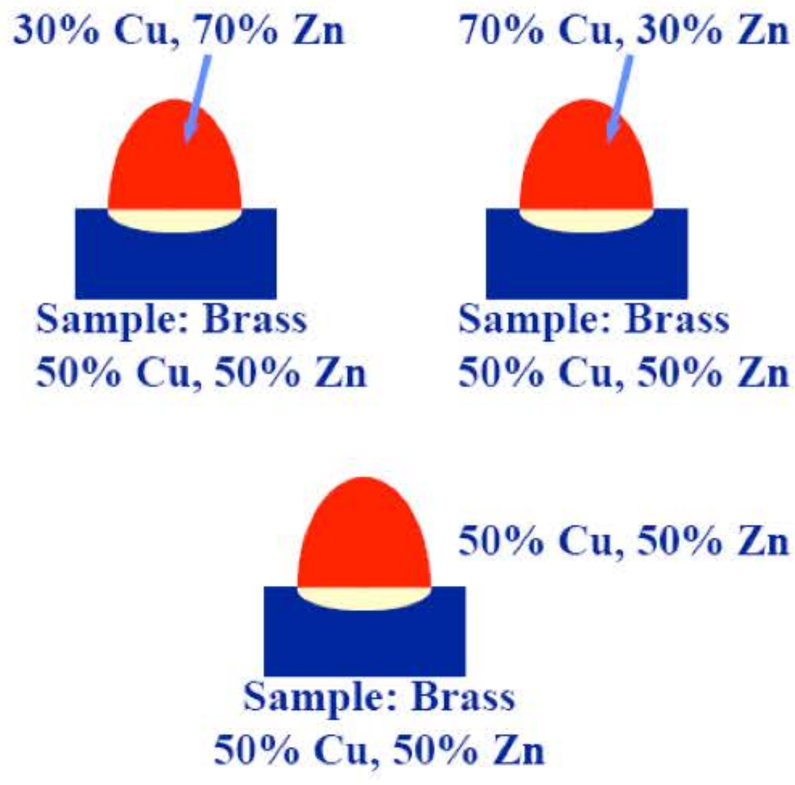
The ablation yield varies for different sample matrices (e.g. the ablation rate is not the same for copper than for glass or polymers...



The ablated mass depends on the laser energy but not linearly : fluence (=> focalisation), pulse duration, etc..

The detected elemental composition of the ablated mass might depends on the laser energy (elemental fractionation)

We will see later how to identify the elemental fractionation, how to calculate it and what are the physical processes behind it... And eventually how to counterbalance it or at least limit it...

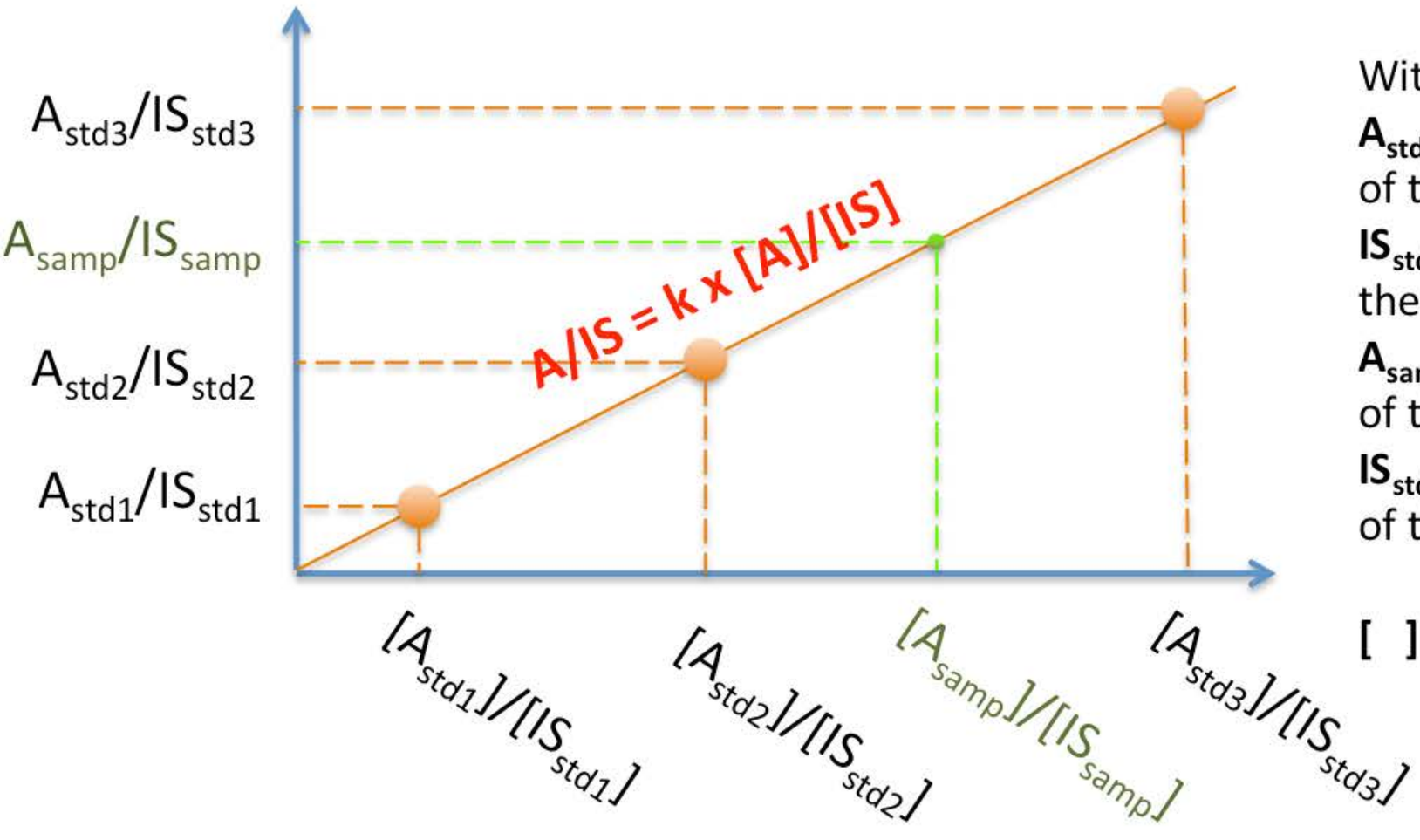


Adapted from R. Russo – Winter conférence 2004

Quantification: External calibration with internal standard

The quantification of a sample is generally carried out by external calibration using standards of similar matrix. For synthetic materials (glass, etc..), numerous standards are commercially available.

Bias resulting from laser ablation processes (laser energy drift, focussing problems, sample transport, etc...) and the ICPMS can be corrected using an Internal Standard (a given element that we know the concentration in the standard AND the sample). The IS must be homogenously distributed (generally part of the matrix) as it is used for normalisation. The IS in the sample can be obtained by XRF measurement for instance.



With

$\mathbf{A_{stdi}}$: NET (blank corrected) signal intensity of the Analyte for standard i

$\mathbf{IS_{stdi}}$: NET (blank corrected) signal intensity of the Internal Standard for the standard i

$\mathbf{A_{samp}}$: NET (blank corrected) signal intensity of the Analyte for the sample

$\mathbf{IS_{stdi}}$: NET (blank corrected) signal intensity of the Internal Standard for the sample

[ ] Concentration

Internal standard normalised calibration curve

Quantification: External calibration with internal standard

Then, knowing the concentration of IS in the sample, the concentration of the analyte in the sample is expressed as follow :

$$[A]_{samp} = \frac{\frac{A_{samp}}{IS_{samp}} \times [IS]_{samp}}{k}$$

This equation WORKS ONLY IF the internal standard behaves similarly as the analyte in terms of laser/material interaction AND particle atomisation in the ICPMS.

For natural samples, it is not always true due to the wide range of matrices and the lack of Certified Reference Materials (CRM). This makes the quantification more challenging...

Quantification: Evidence of Elemental Fractionation

Ideally, when ablating a homogenous sample, all the elements should have the same signal profile. In fig A, a crater was drilled in CRM NIST610 (glass). It is clear that Ca and U exhibit quite similar profiles (the progressive signal extinction is due to laser fluence drop as the crater becomes deeper. One can also imagine that particles are less efficiently removed from the bottom of the crater). However, Pb profile departs from Ca and U **which indicates that all the element don't behave similarly**. **This calls into question the use of an internal standard to correct for ablation processes drift, especially when the sample matrix differs from the standards one... The quantification is directly affected** as illustrated in figB, even after internal normalisation (here Ca) as the calibration slopes differ from glass to $CaCO_3$...

THIS IS THE ELEMENTAL FRACTIONATION....

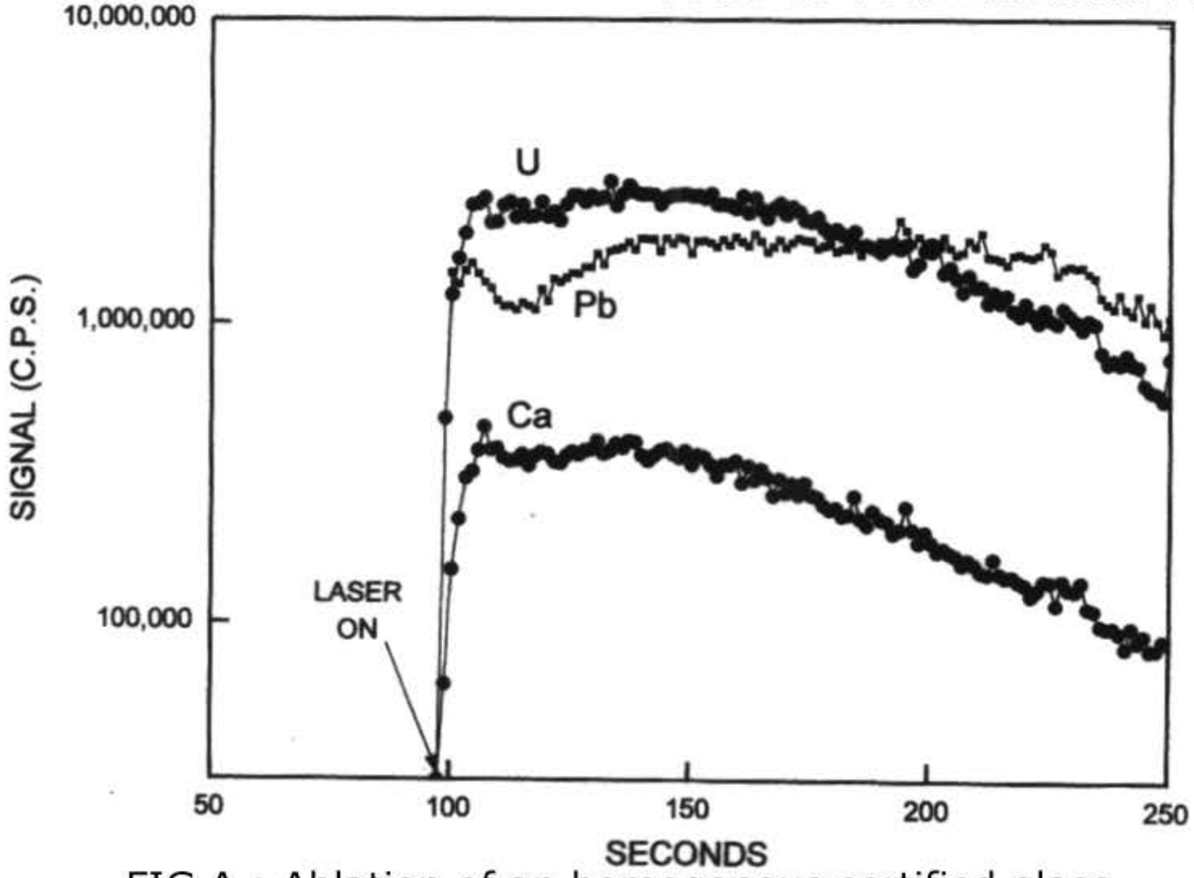


FIG A : Ablation of an homogenous certified glass sample (NIST 610). ns 266 nm laser

D. Gunther et al, Spectr. Chim. Acta, 1999, 54, 381-409

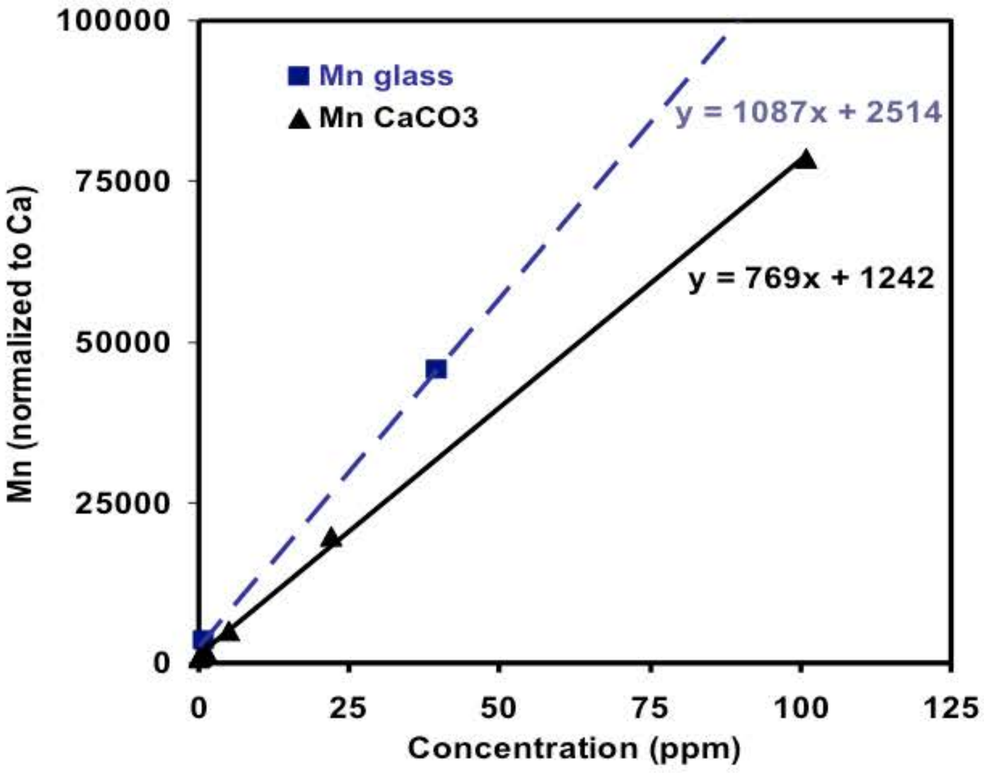


Fig B Calibration with certified **glasses** and **$CaCo_3$** standards. ns 266 nm laser

A. Barats et al, PhD thesis - 2006

Quantification: Origin of the elemental fractionation

Two main processes can explain the elemental fractionation

1/ **Selective evaporation** : It appears as a result of the **laser/material interaction** where the **vapour phase is enriched** with some **elements** with **low sublimation enthalpy** : this is then a **non stoichiometric sampling** where the aerosol composition (particles + vapor) does not reflects the sample composition...
It is governed by the ablation conditions (temperature, the time duration of the interaction, induced plasma, the surface of interaction, etc...) and the physical properties of the sample. Melting and melted material deposited around the crater enhance this phenomenon.

This fractionation affects mostly siderophile elements (Zn, Pb, Au, Tl) whereas refractory elements (Ca, U, Th, rare earth) are less affected.

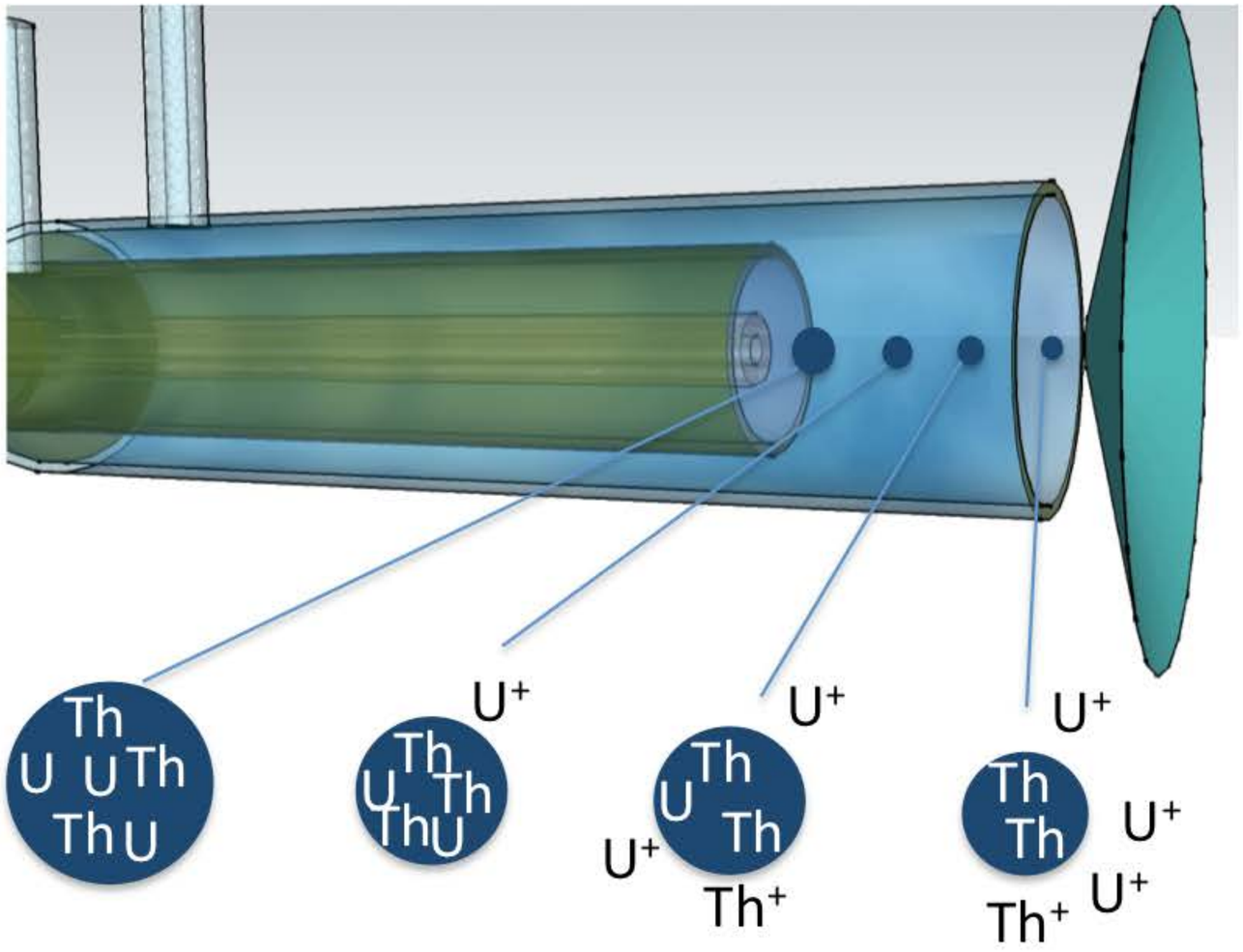
Over the course of the ablation, the sample is more and more heated (as the induced plasma interacts with the crater wall) which generated the vapor enrichment with "volatile" elements : this fractionation can be evidenced by monitoring the ratio of a "volatile element" versus a refractory element (Pb/U) : the ratio starts from a "true" value that progressively increases.

By using shorter laser wavelength (deep UV), these thermal effects (and then the fractionation indexes) are much less pronounced which explain the success of 193 nm, 213 nm or 266nm lasers.

$$FI_{1064nm} > FI_{266nm} > FI_{213nm} > FI_{193nm}$$

Quantification: Origin of the elemental fractionation

2/ Particle size: Incomplete atomisation of the laser induced particles, **into the ICP**, has been proposed more recently. Here the fractionation does not occur at the ablation site, but in the plasma of the ICPMS, the **biggest particles being less efficiently atomised (>150 nm)** than the smallest.
In these hot plasma conditions (7500 K), the most volatile elements contained in the particle diffuse more rapidly than the most refractory which generates a bias if the particle is not completely atomised : the remaining particles are then highly enriched in refractory element that will never be ionised (and then detected).

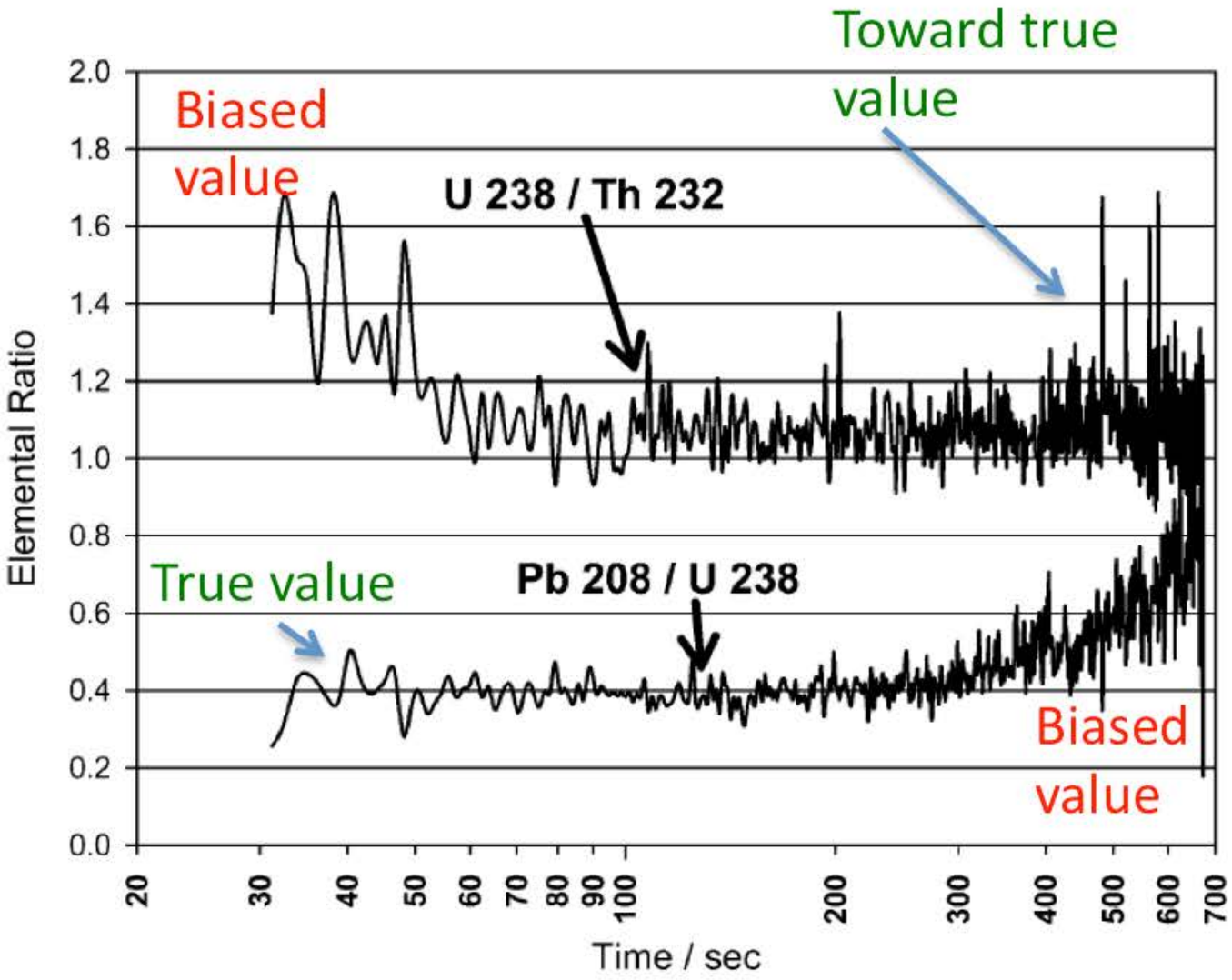


This is illustrated here with U (heat of vaporisation=417 kJ.mol^{-1}) and Th (heat of vaporisation=514 kJ.mol^{-1})

This phenomenon is also indirectly governed by the laser wavelength since the particles size distribution is shifted towards smaller particles when using short wavelengths (see below).

Quantification: Origin of the elemental fractionation

During the ablation, the particle size distribution changes; big particles (up to 2µm) being produced during the first pulses whereas smaller particles are gradually produced. The U/Th ratio is then biased at the beginning and tends towards true value at the end of the ablation.



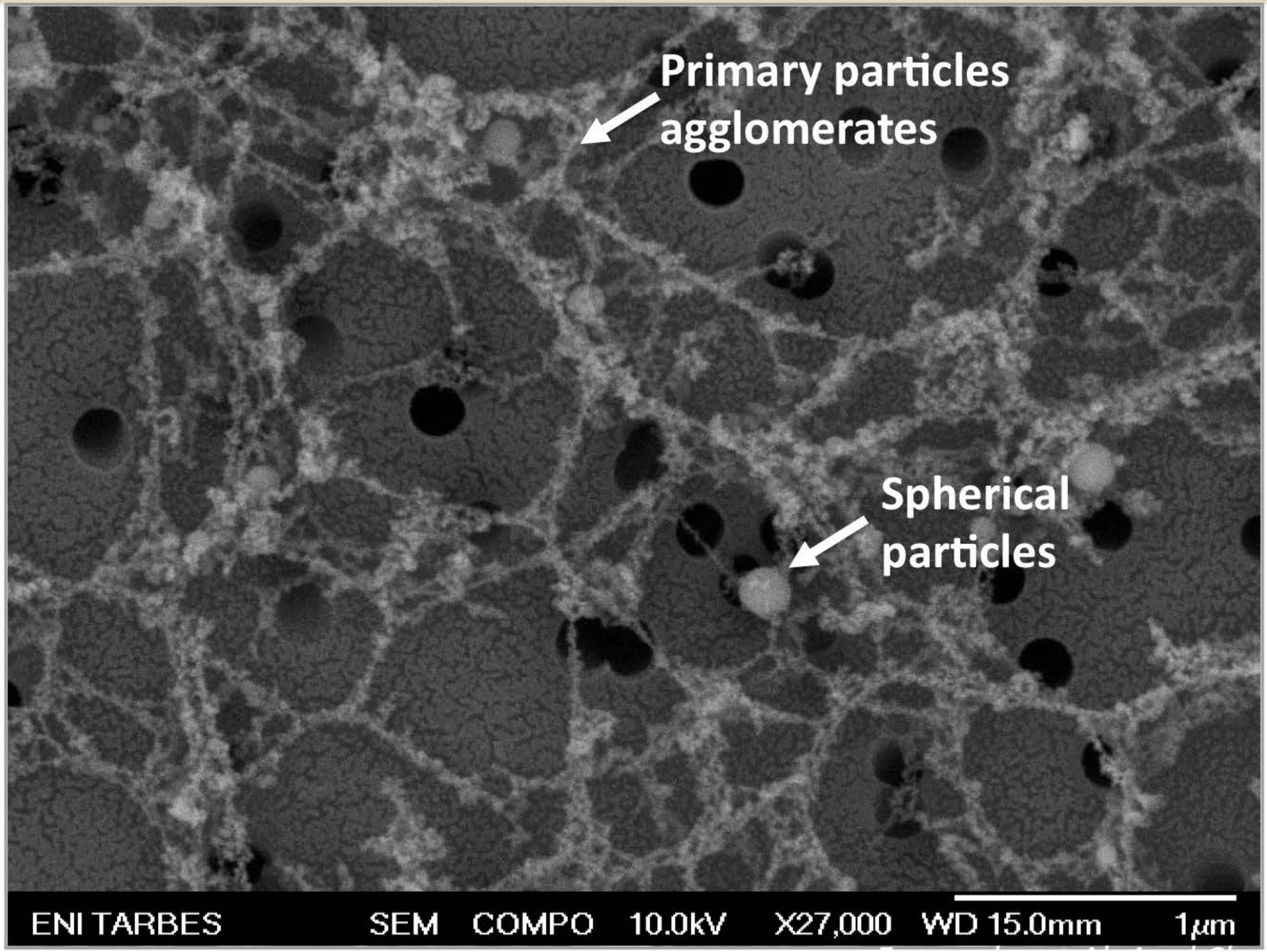
Adapted from Guillong et al, J. Anal. At. Spectrom., 2003, 18, 1224–1230

Robust ICP conditions (High power, low carrier gas, etc...) allow reducing this elemental fractionation (but it depends also on the instrument).

U and Th in the NIST 612 (or 610) are generally used for tuning the ICP since:

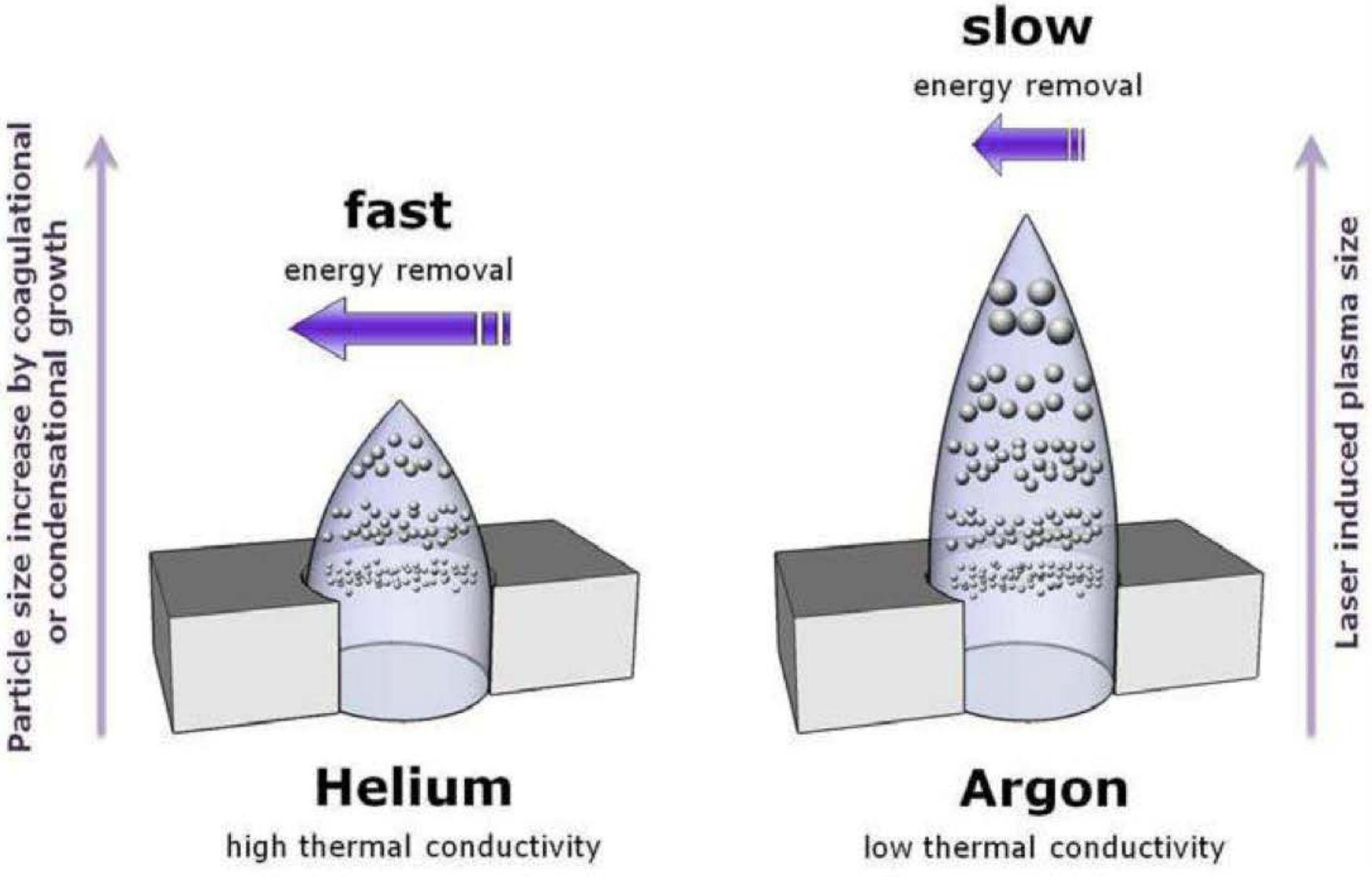
- 238U and 232Th have similar masses (they are then similarly affected by space charge effect).
- U and Th have similar ionisation potential (6,2 and 6,1 V respectively).
- [U]=[Th] in these sample U/Th=1

The key is the particle formation…



The key is the particle formation…

1/ Primary particles generation : => Vapour phase condensation-Coagulation



Particles <100 nm depends on:

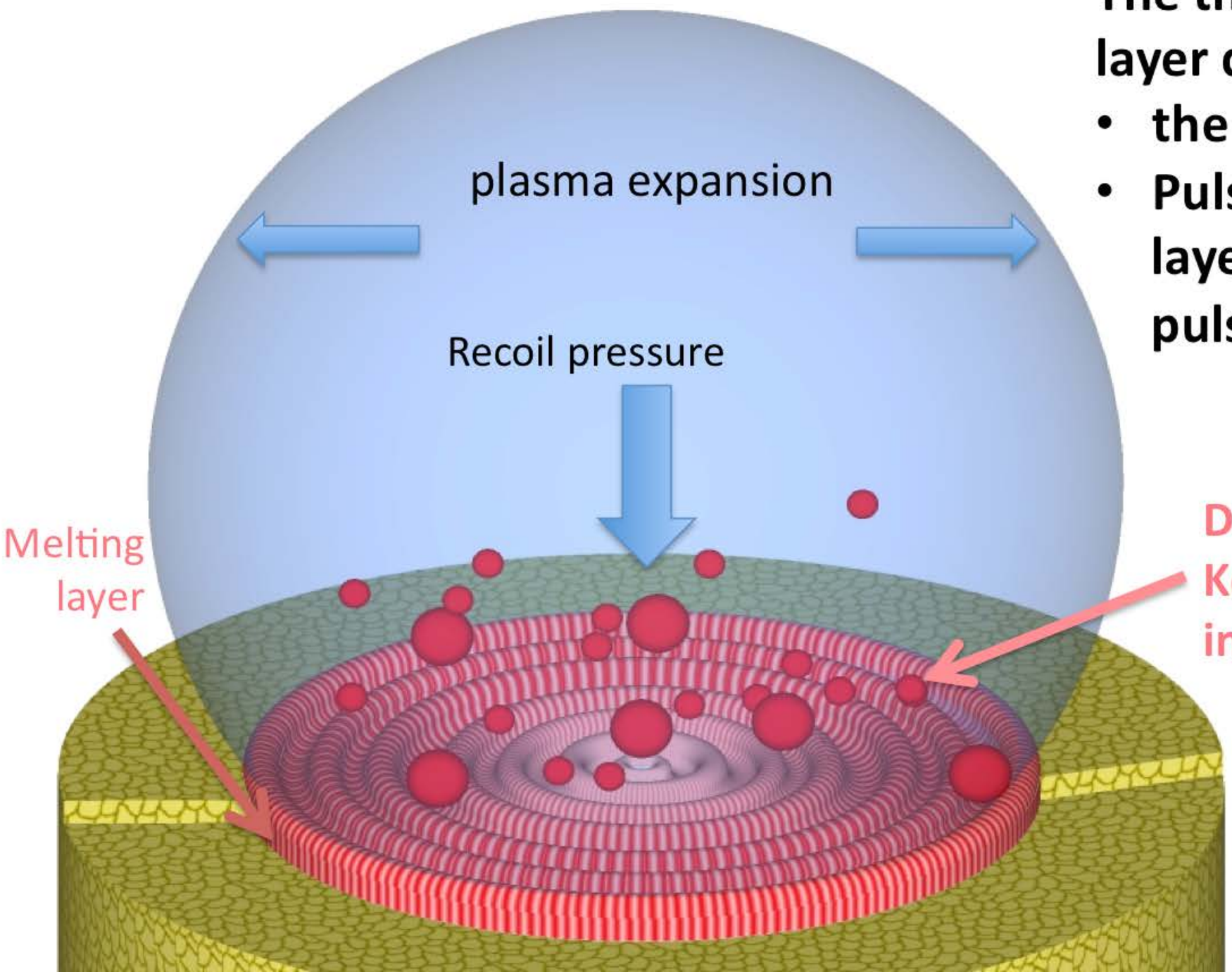
- **Pressure**
- **Surrounding gas**
- **sample**

Adapté de Horn et al Applied Surf. Sci. , 2003

The key is the particle formation…

2 – Hydrodynamic sputtering (spherical particle>100 nm)

More info in Hergenroeder J. Anal. At. Spectrom., 2006, 21, 517–524 | 517

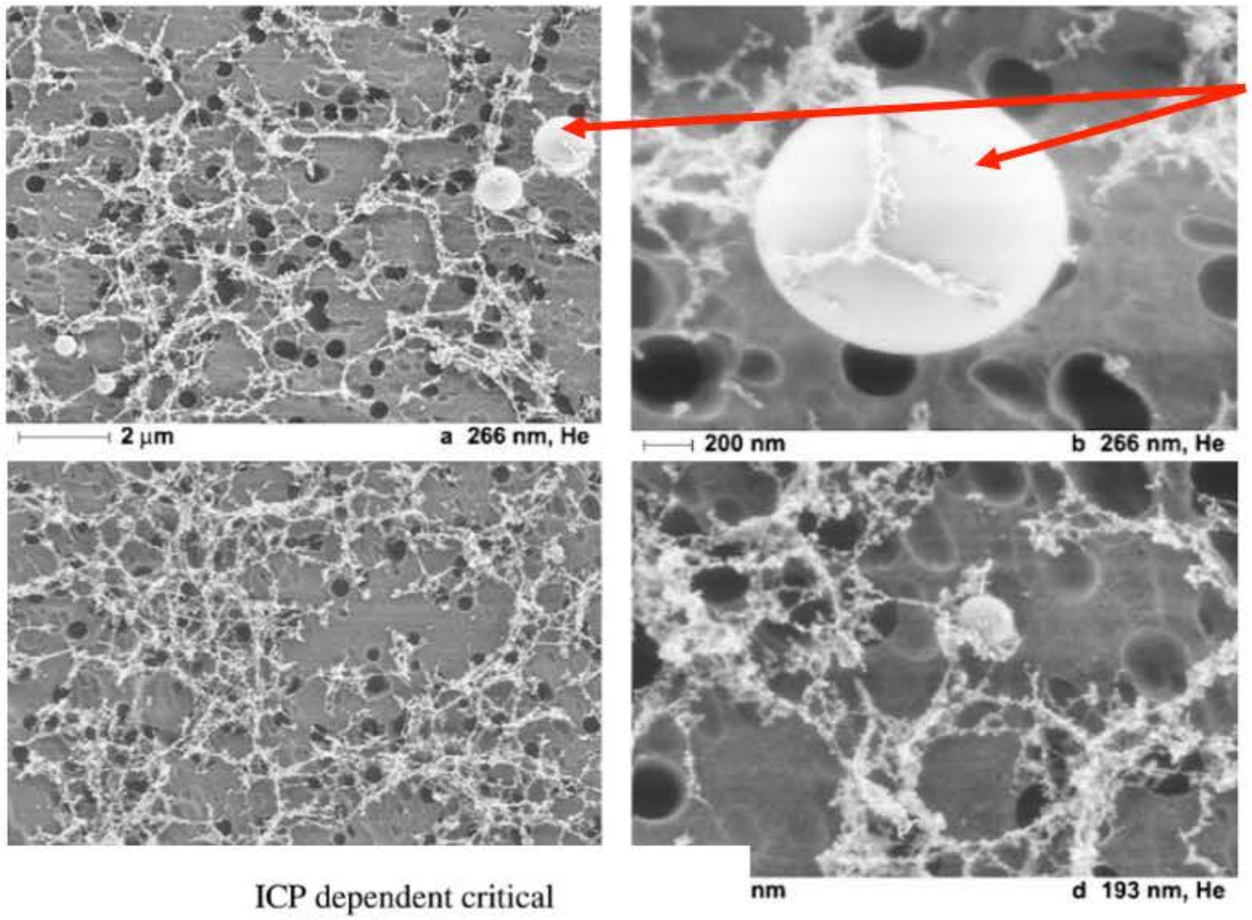


The thickness of the melting layer depends :

- **the wavelength**
- **Pulse duration (very thin layer with femtosecond pulses)**

Schéma d'artiste

The key is the particle formation…



Melted material

266 nm UV laser

Transparent glass sample
(NIST 610)

193 nm UV laser

H. Kuhn et Al, abc, 2005,383,434-441

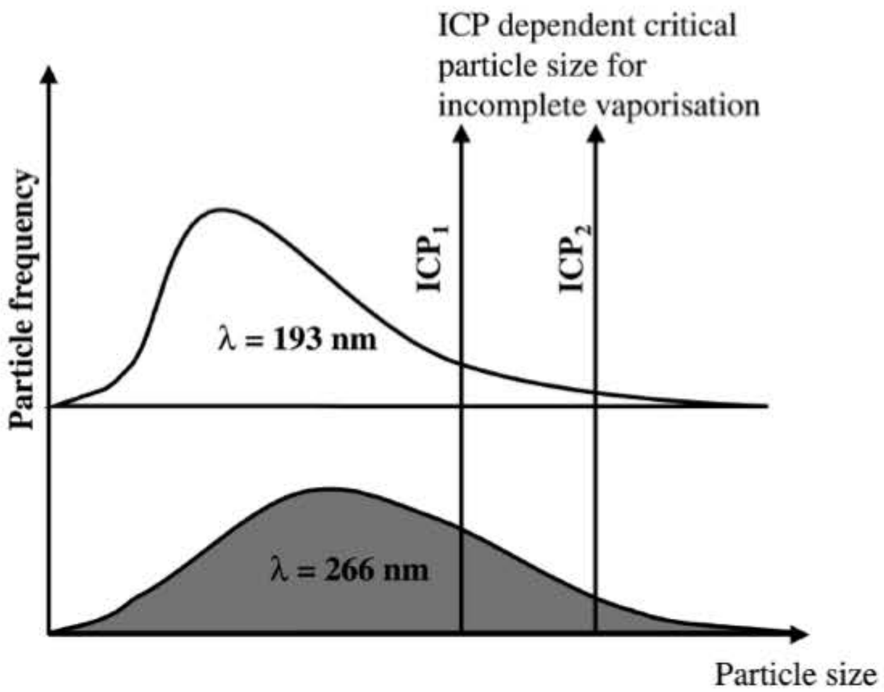


Fig. 12 Schematic diagram of influence of ICP conditions on incomplete particle vaporisation and the contribution of the latter to elemental fractionation.

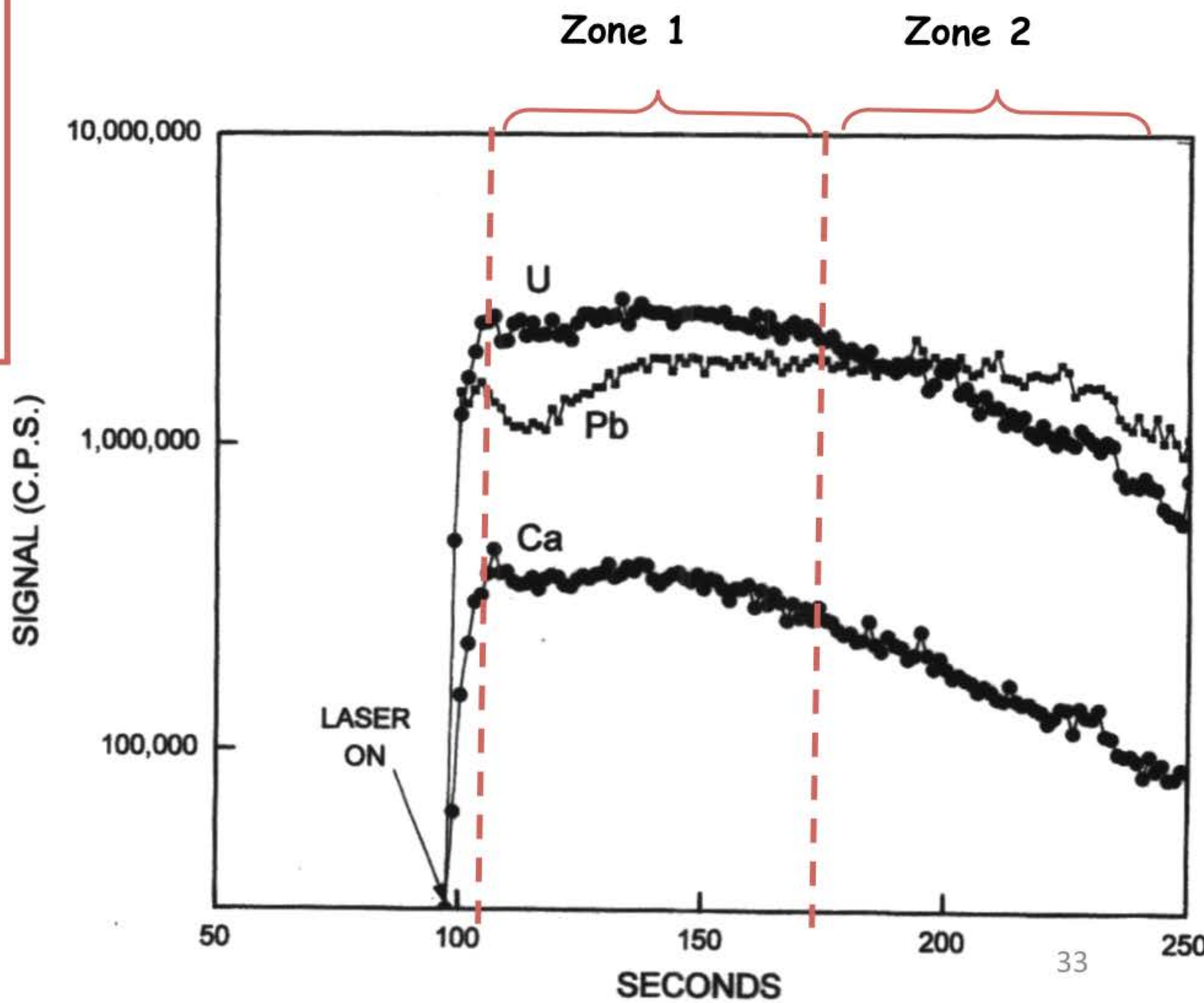
The aerosols is consituted by agglomerated primary particles and spherical particles resulting from melting. At 266 nm more spherical particles (and also bigger) than at 193 nm,

M. Guillong et Al, JAAS, 2002,17,831-837

How to quantify the elemental fractionation…

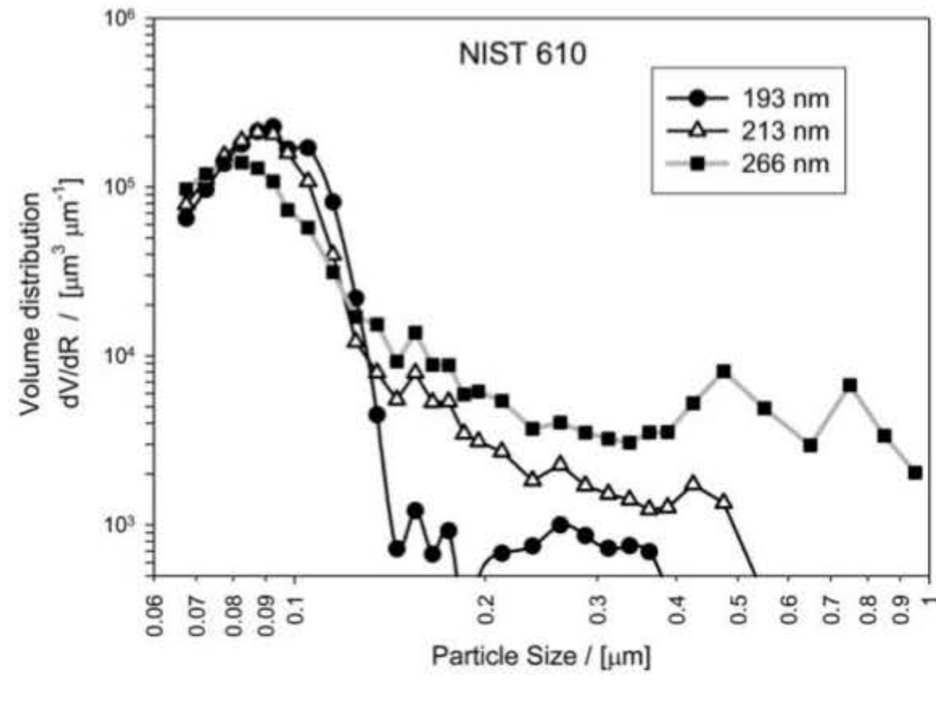
For a given analyte, the fractionation index (FI) is defined with respect to another element taken as reference (generally Ca or Si). It reports the variation of the ratio over the course of the ablation taking into account 2 zones

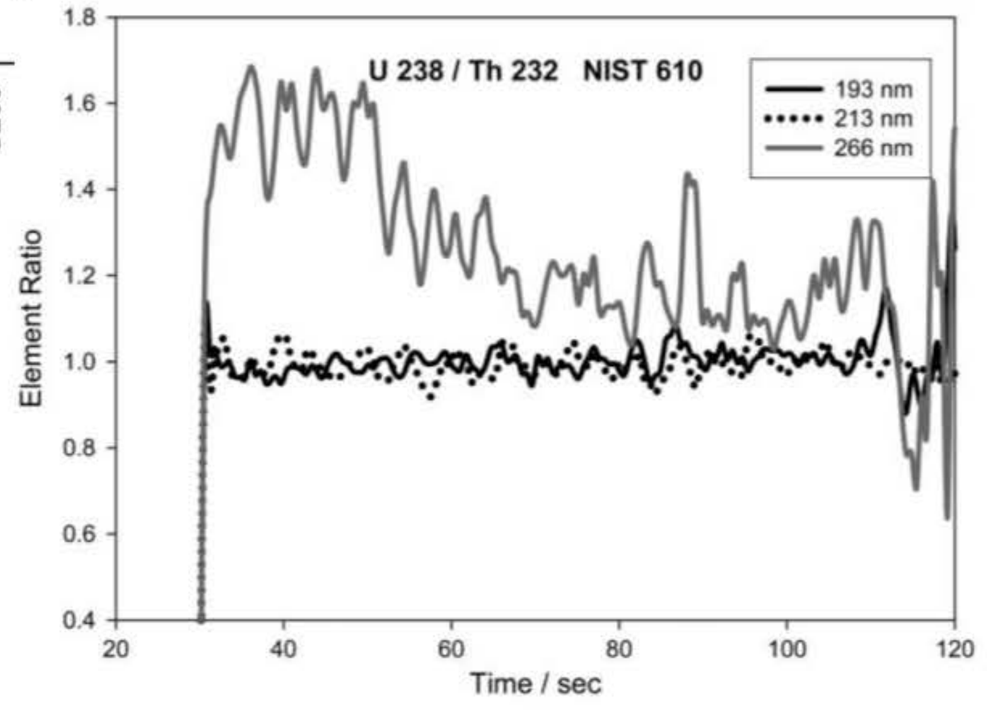
$$FI_{Pb/Ca} = \frac{\langle Pb \rangle_{zone1} / \langle Ca \rangle_{zone1}}{\langle Pb \rangle_{zone2} / \langle Ca \rangle_{zone2}}$$



The fractionation index depends on the sample…

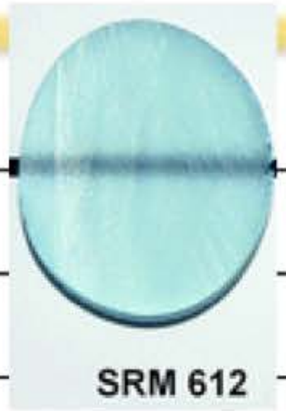
$FI_{266nm} > FI_{213nm} > FI_{193nm}$

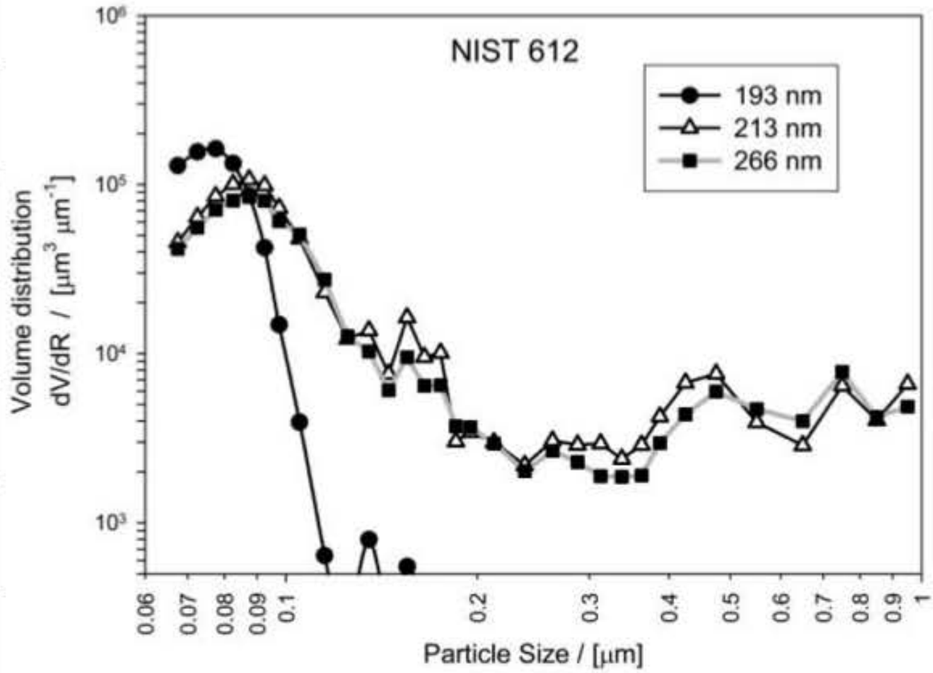




Guillong M. Horn I. Gunther D. A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd : YAG laser for laser ablation ICP-MS. Journal of Analytical Atomic Spectrometry. 18(10):1224-1230, 2003.

The fractionation index depends on the sample…

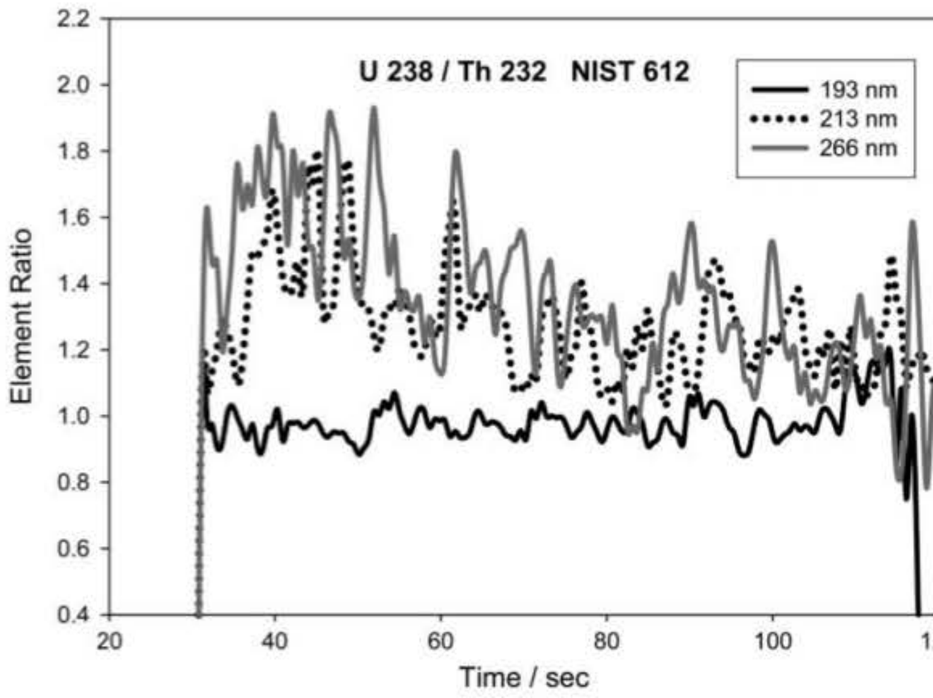




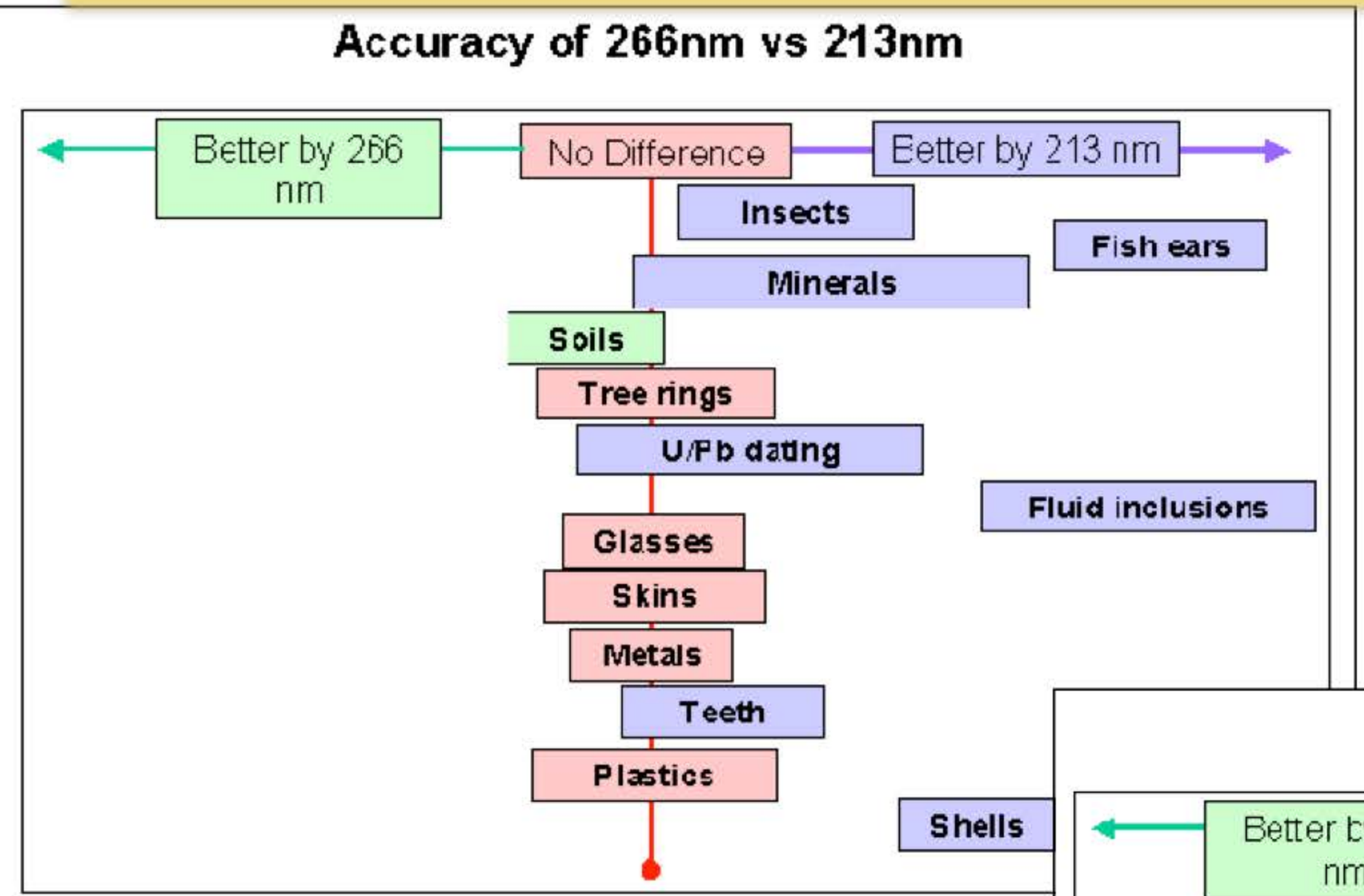
FI generally worse for transparent glasses

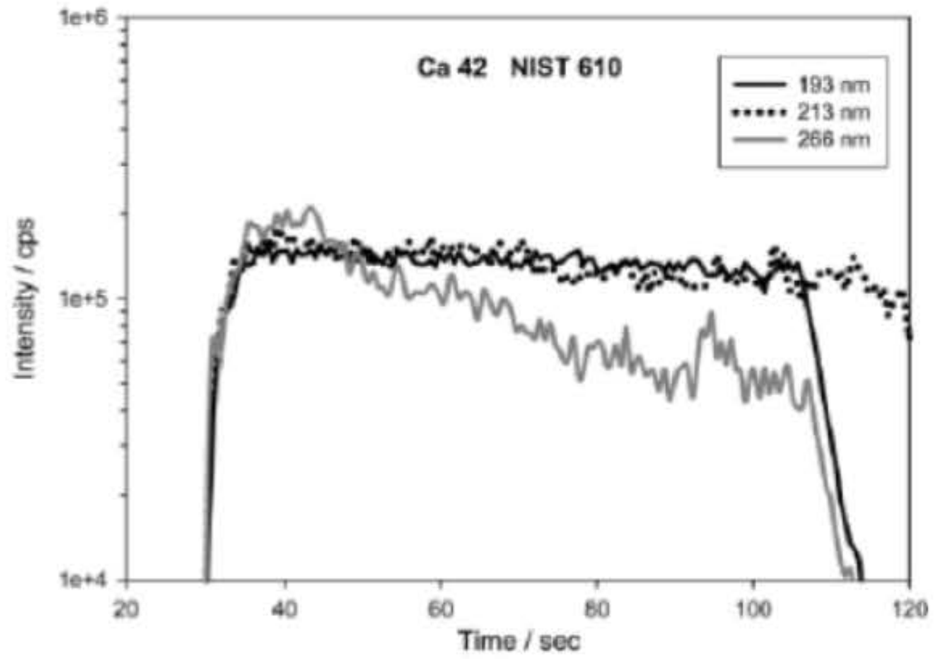
$$FI_{266nm} > FI_{213nm} > FI_{193nm}$$

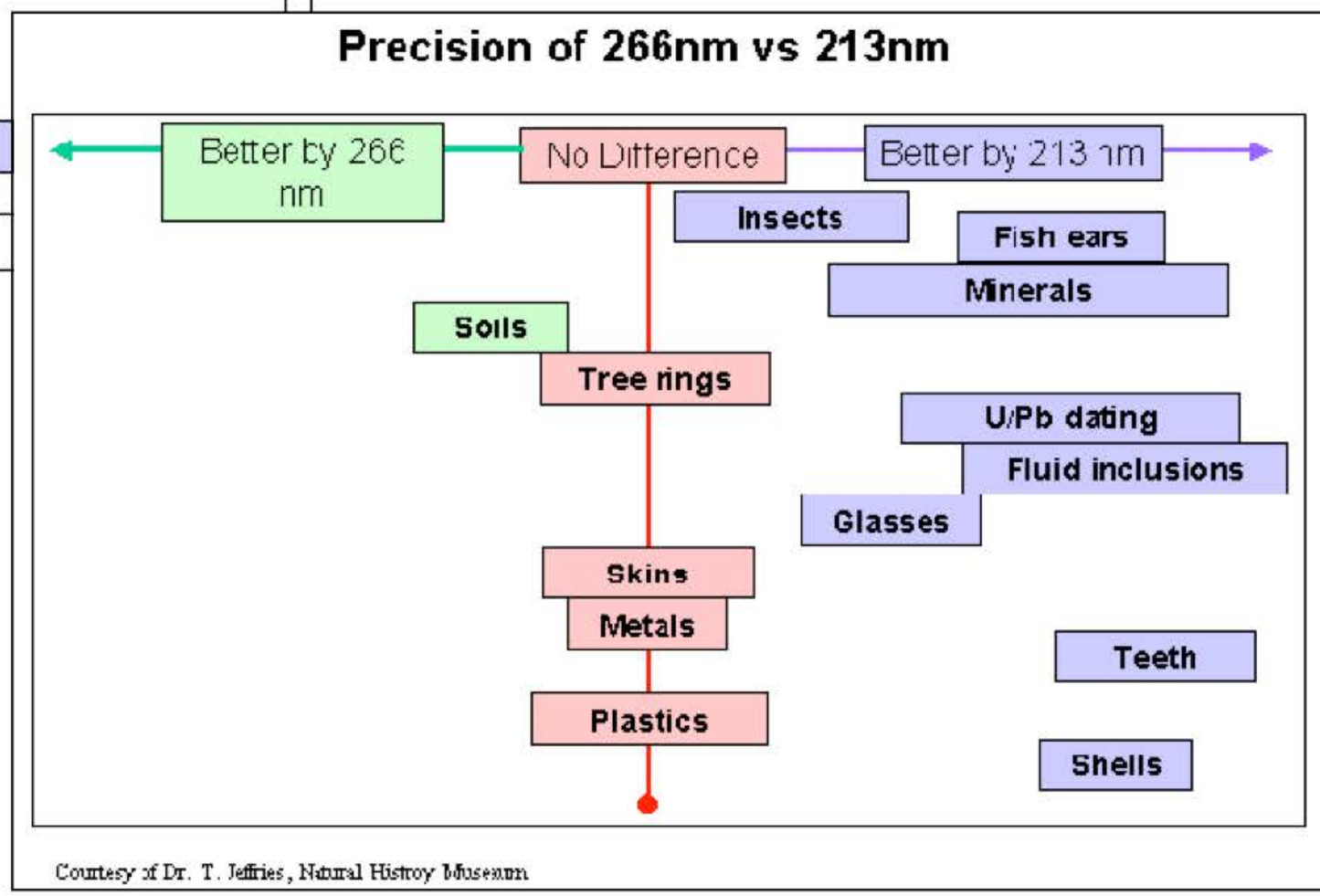
Guillong M. Horn I. Gunther D. A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd : YAG laser for laser ablation ICP-MS. Journal of Analytical Atomic Spectrometry. 18(10):1224-1230, 2003.



213 nm vs 266 nm lasers







Solutions for elemental fractionation…

ELEMENTAL FRACTIONATION
=
Non stoichiometric detection

Solution?

Matrix Matching using certified reference material

⇒ similar fractionation in the sample and the standard

Using less fractionating lasers

=> Deep UV,
=> Fluence
=> Power density,
=> Ultra short pulses (fs), Etc...

Tuning the LA/ICPMS

Tuning of the LAICPMS coupling :

- According to “normal” ICPMS recommendation in liquid configuration
- **Efficient particles atomization**

Use a NIST 612 glass sample and set the ICP parameters in order to get **U/Th =1 ±0,05** (theoretical value U/Th=1).

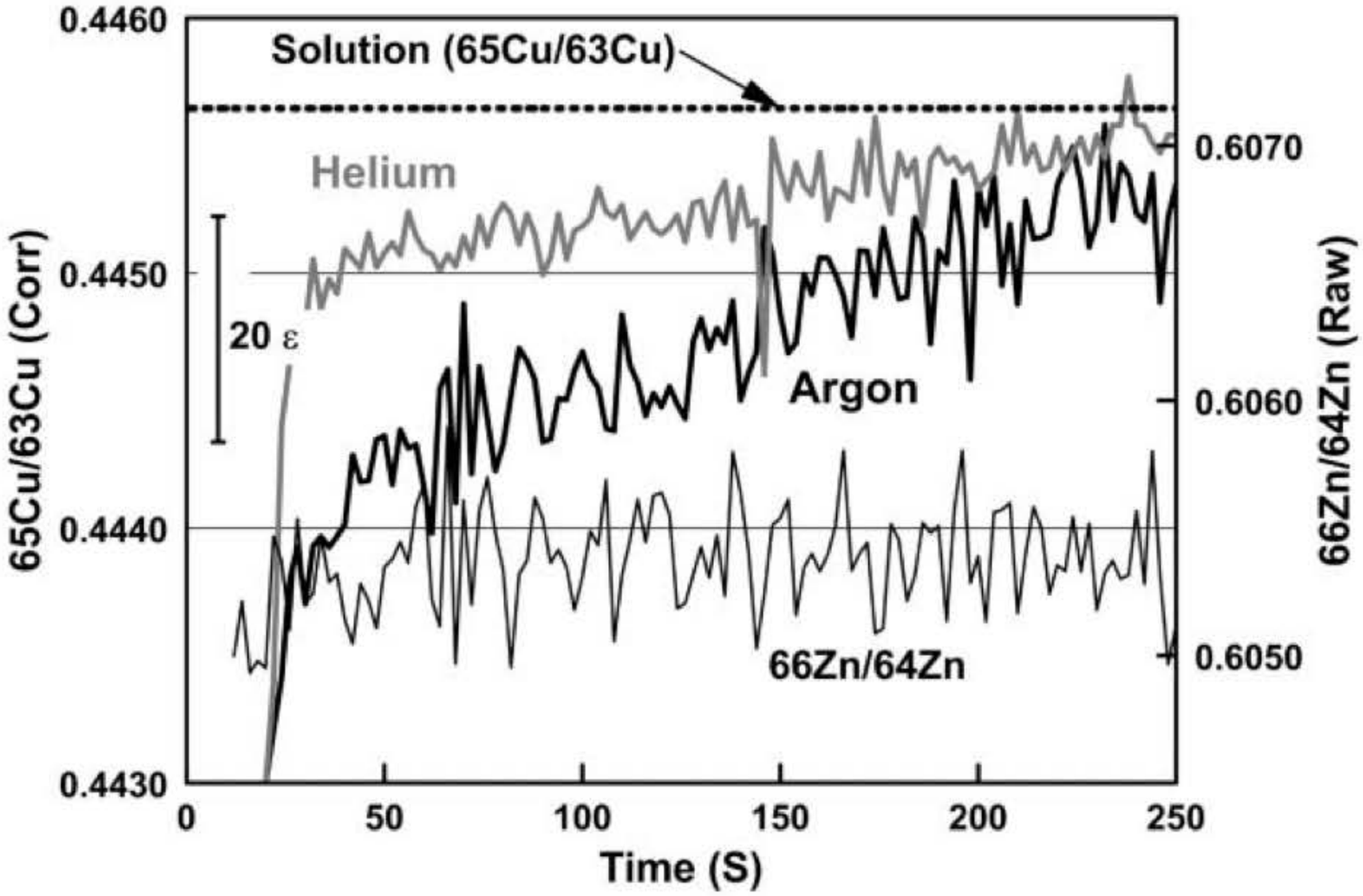
The U/Th ratios tend to be higher than 1 due to incomplete particles atomization.

Robust ICP conditions are mandatory to reach accuracy. They are very often obtained while sacrificing signal sensitivity, and vary from one instrument to the other :

- High power (>1200W)
- Reduced carrier gas flow (compared to the optimal signal sensitivity conditions)
- Reduced auxiliary gas

Isotope fractionation

nsLA/MC-ICPMS of chalcopyrite



Like elemental fractionation, isotope fractionation occur also. It is mainly attributed to incomplete particles atomisation and faster diffusion of light isotopes...

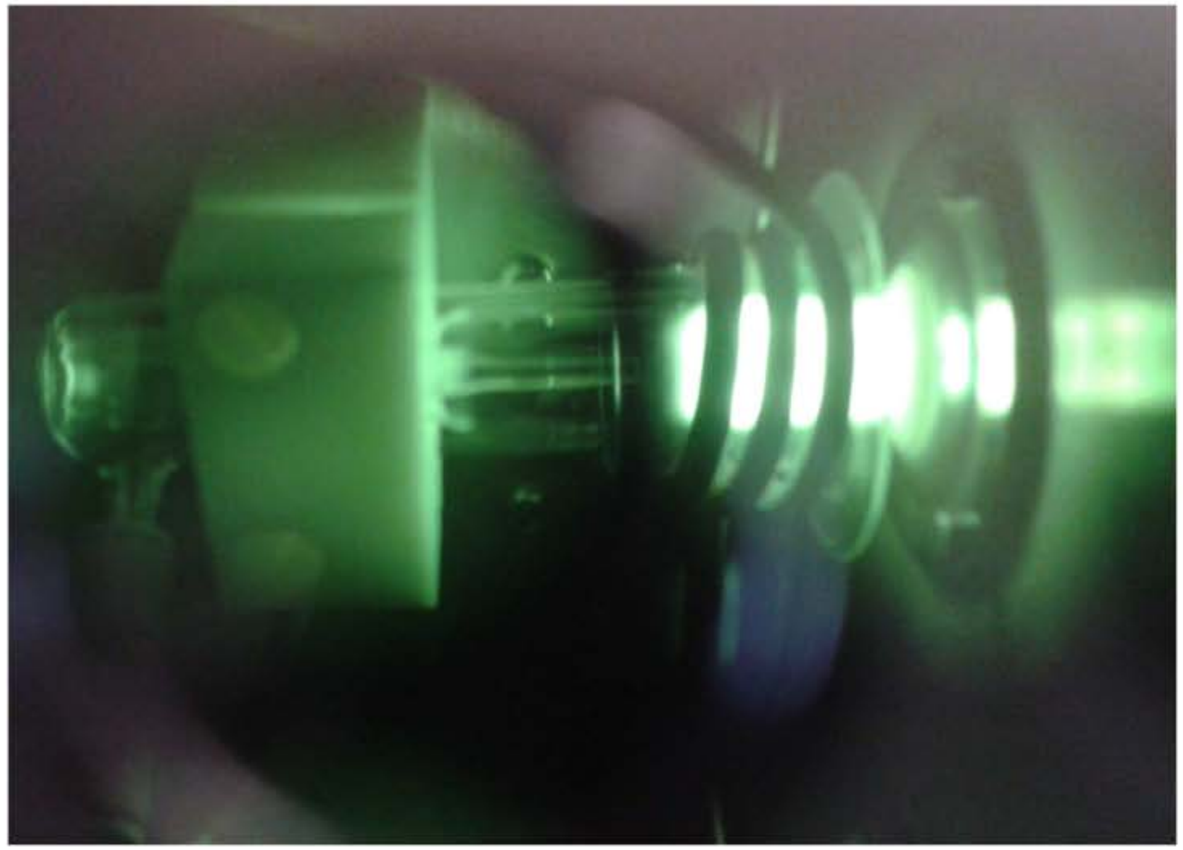
Fig. 1 Time resolved 65Cu/63Cu ratios, corrected for mass bias, for ablation of chalcopyrite using Ar (bold) and He (light) as ablation gases (ablation commenced at 20 s). The 65Cu/63Cu ratios gradually increased towards the value determined by solution-MC-ICP-MS analysis for the same chalcopyrite sample. The thin line shows the raw ratios for an Ar supported semi-dry Zn aerosol, produced by a desolvating nebulisation system, added to the carrier gas stream during the ablation of chalcopyrite in Ar. The constant 66Zn/64Zn ratio during ablation indicates that the increase in Cu isotope ratios was a laser-induced phenomenon. Data from Botfield (1999) and unpublished.

S. Jackson and D. Guenther, J. Anal. At. Spectrom., 2003, 18, 205–212

Plasma robustness...

- Only particles < 100-150 nm can be efficiently atomised into the ICP
- The ICP can tolerate a finite amount of particles (plasma loading)
- Specific desorption of the species at different places into the plasma

- Need for improving atomisation and ionisation efficiency
- Need for improving the plasma robustness.

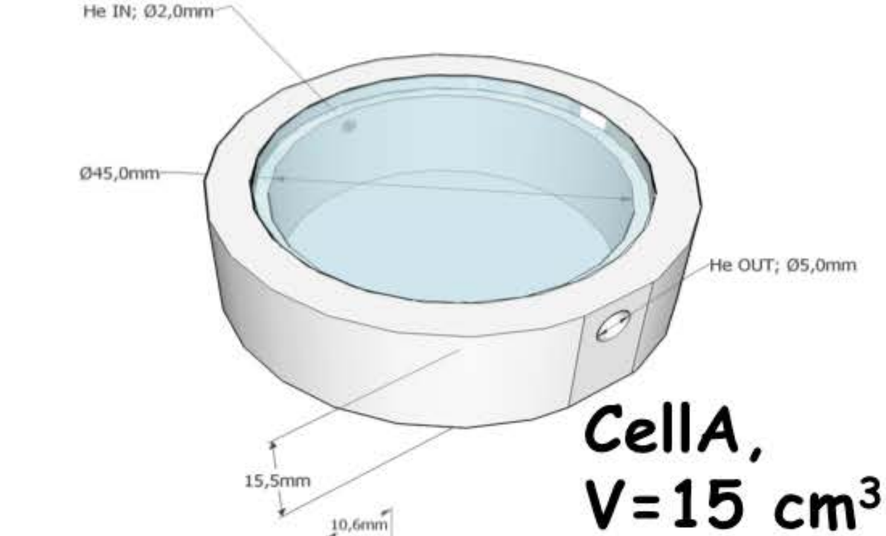


Insights on the ablation cell

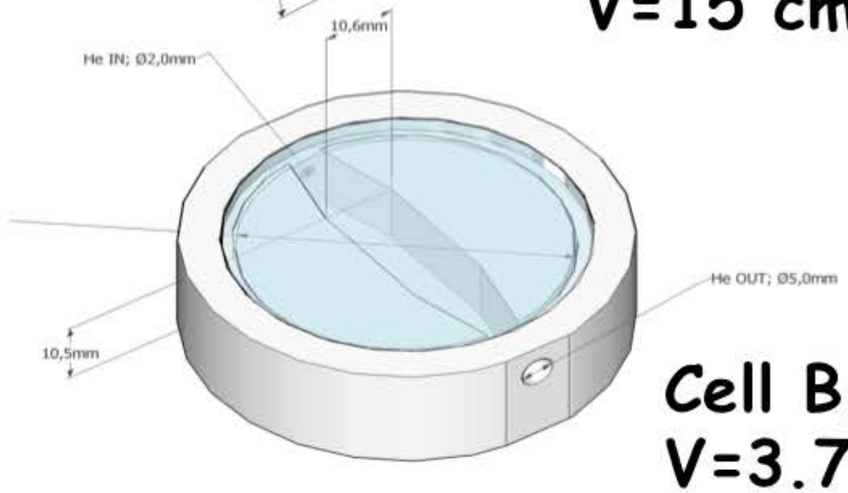
=> Aerosol transport efficiency affects sensitivity and accuracy

=> The finite size of the cell limits the size of the sample

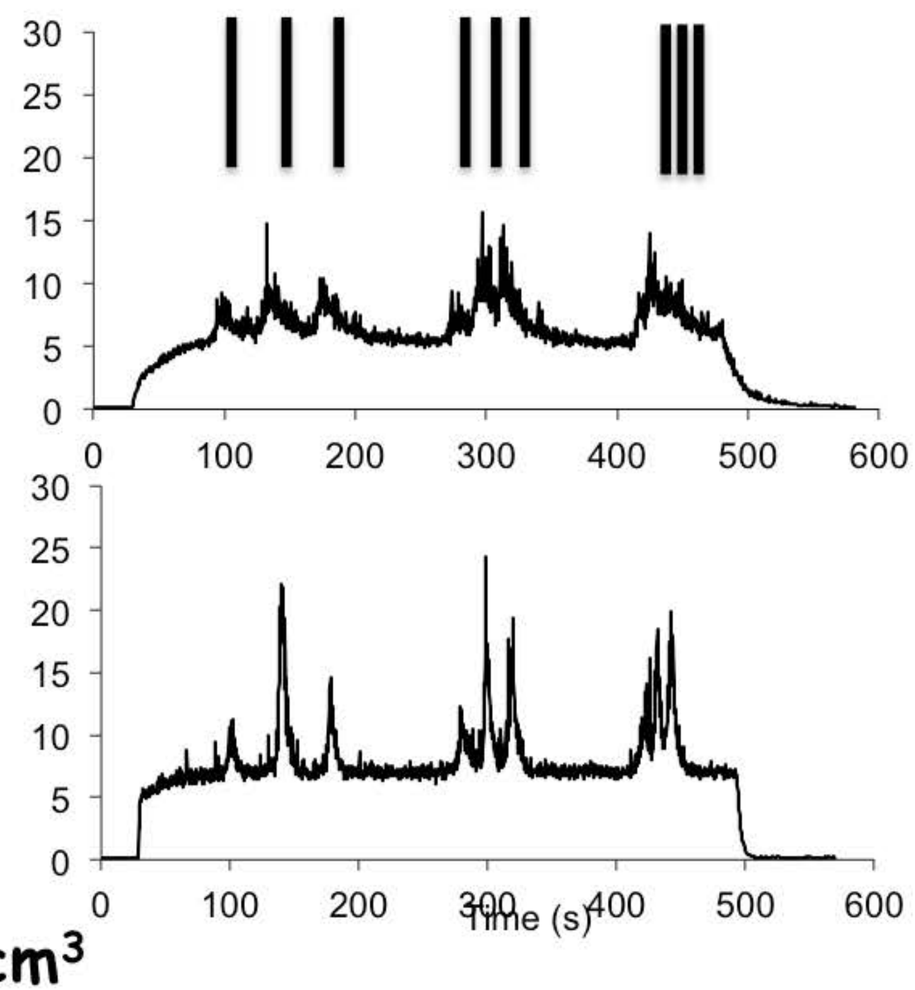
=> Washout time : very important for keeping high spatial resolution (imaging).



CellA, V=15 cm³



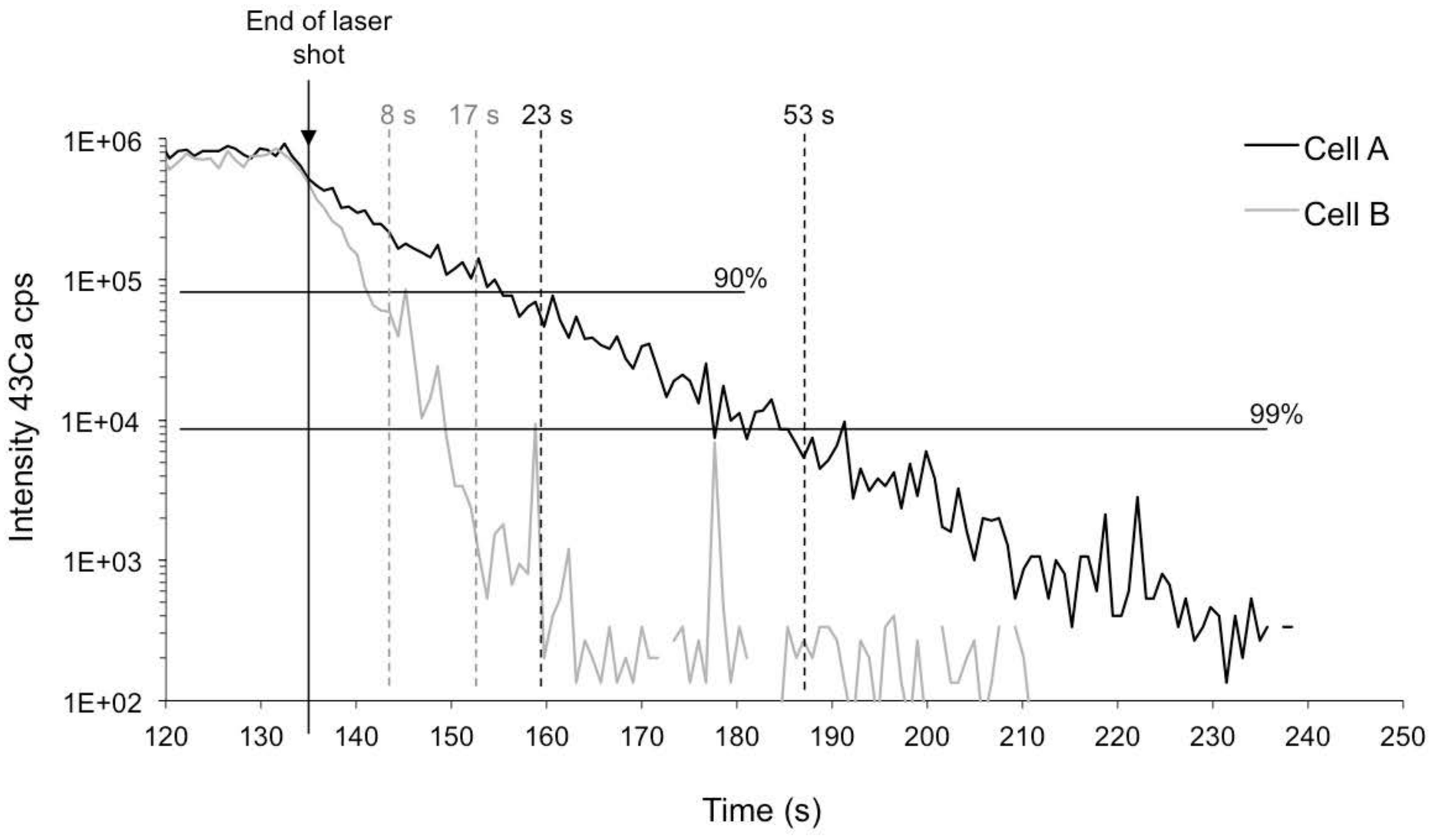
Cell B, V=3.7 cm³



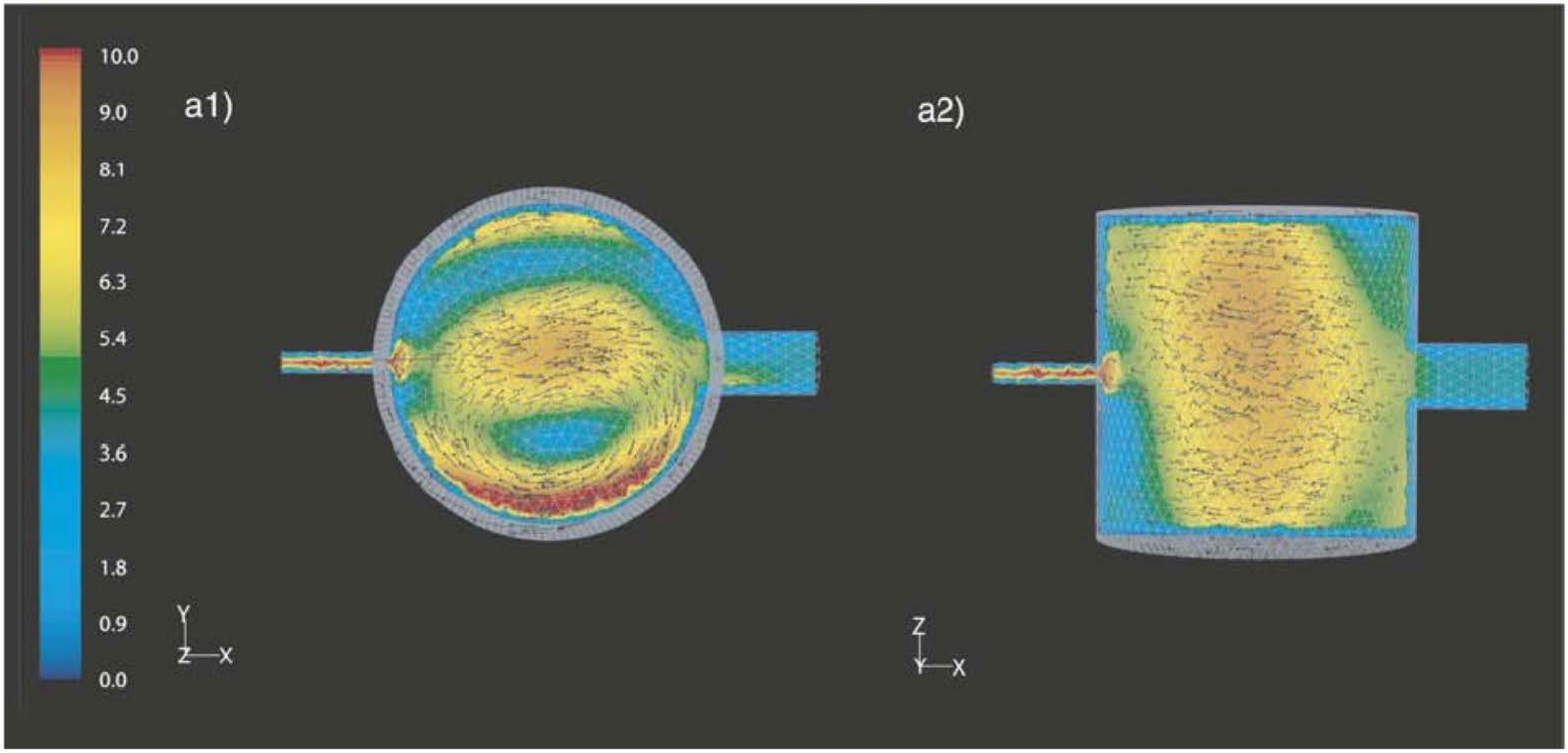
Insights on the ablation cell

The volume of the cell affects:

- spatial resolution in dynamic ablation (scans for instances)
- extraction efficiency and then signal intensity
- Washout time

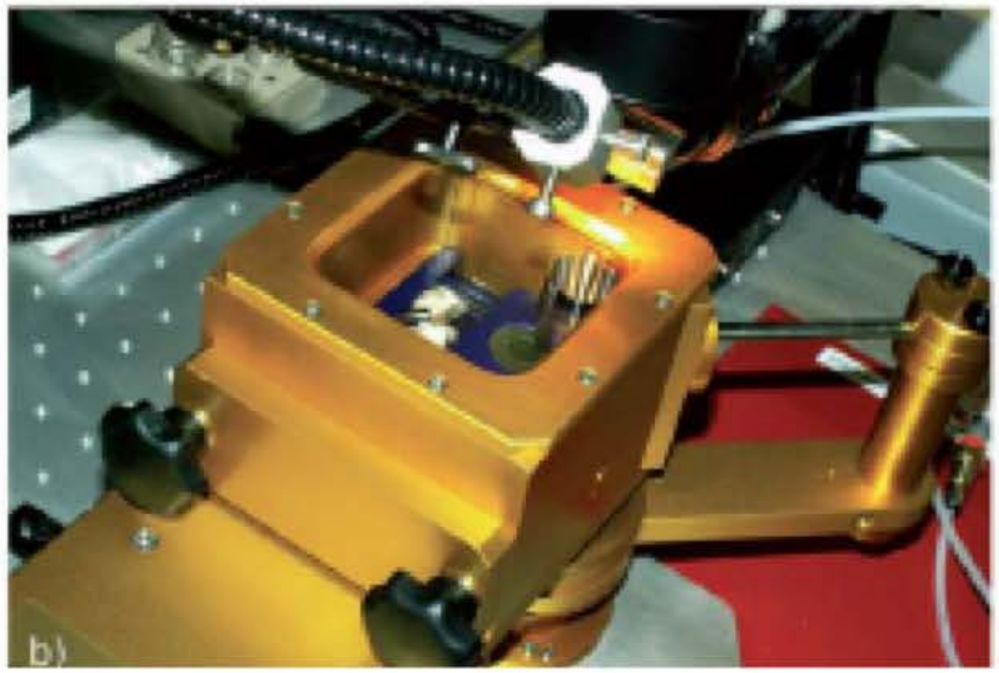


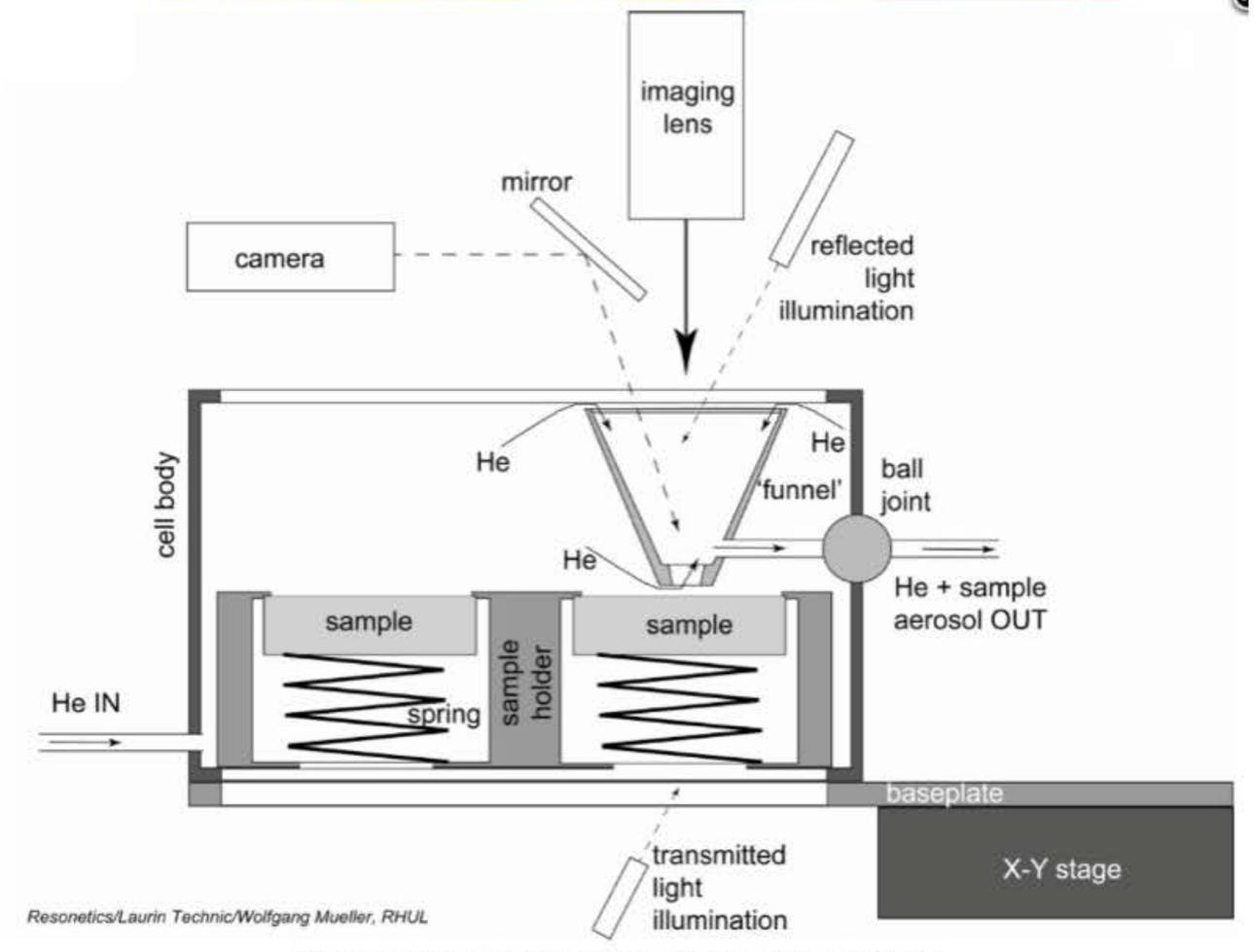
Insights on the ablation cell



D. Bleiner, A. Bogaerts / Spectrochimica Acta Part B 62 (2007) 155–168

Towards mini cells for better washout time



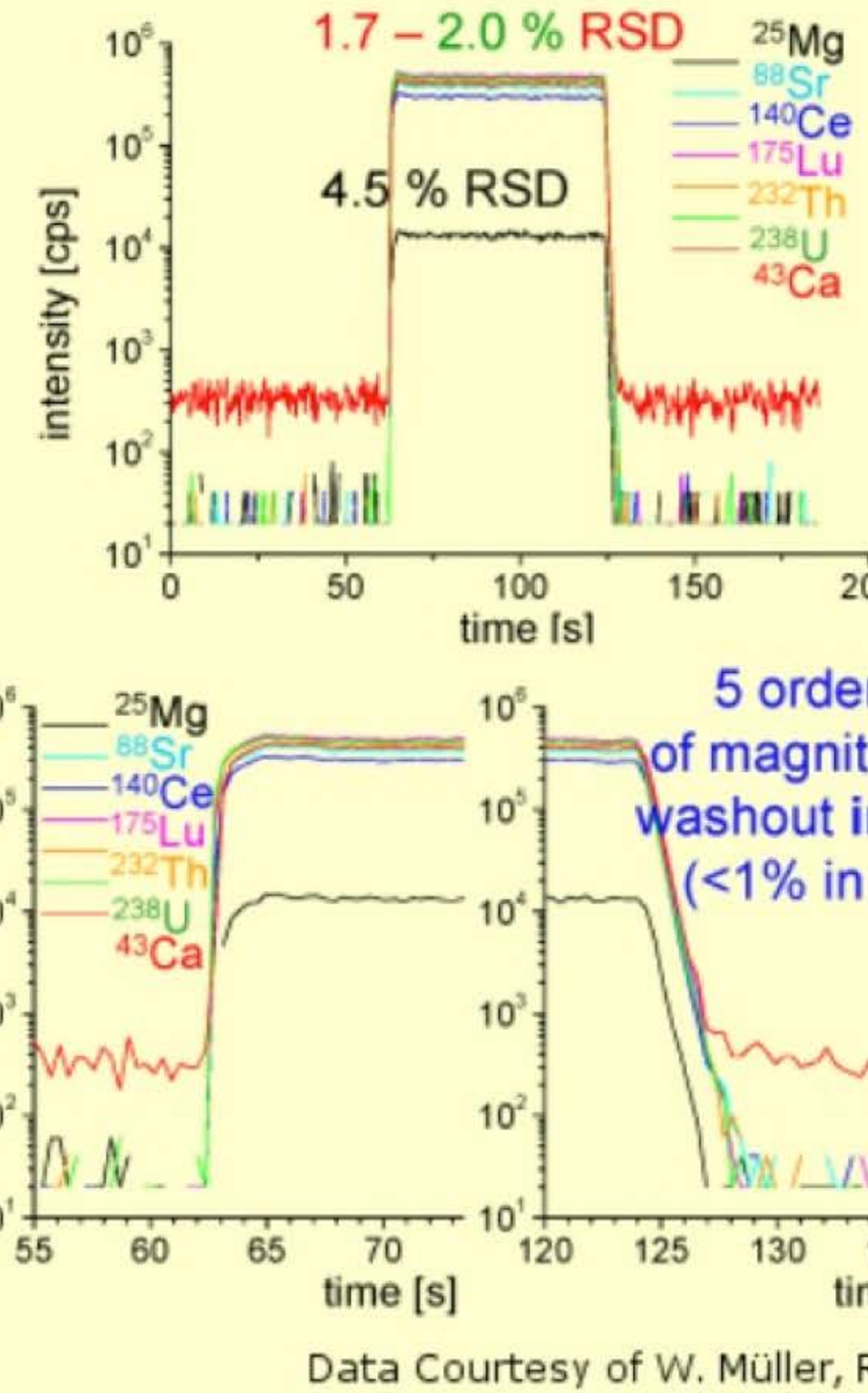


The dual-volume design is an integral part of the M50 and S155 ablation cell design.

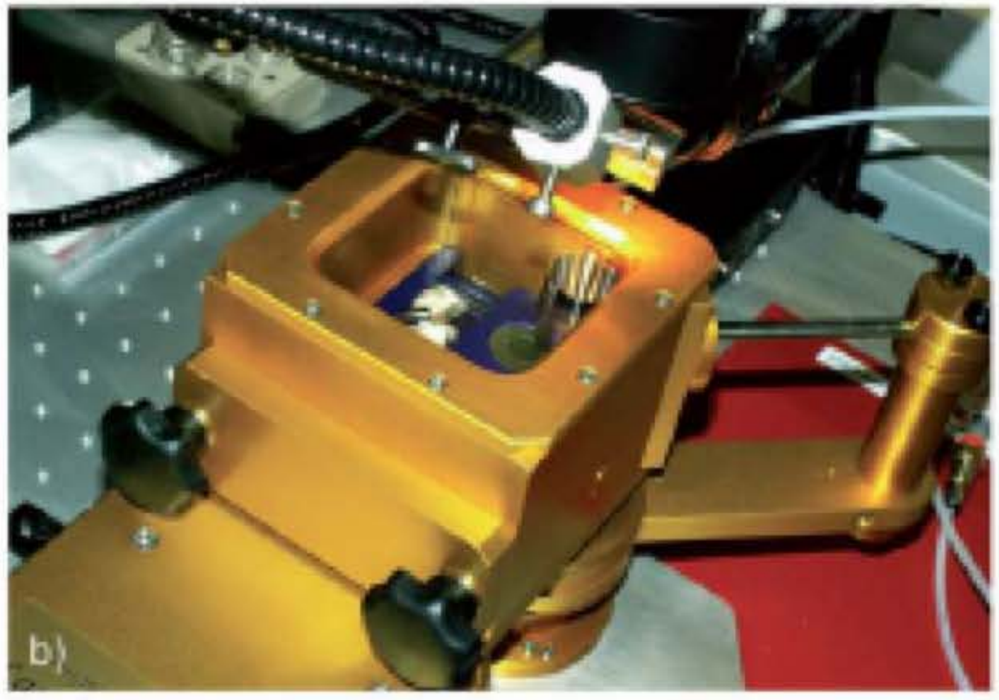
193 nm excimer + 7500ce
74 µm, 10 Hz, He, 4 J/cm², 1mm/min

NIST 612

No 'squid' smoothing



Towards mini cells for better washout time



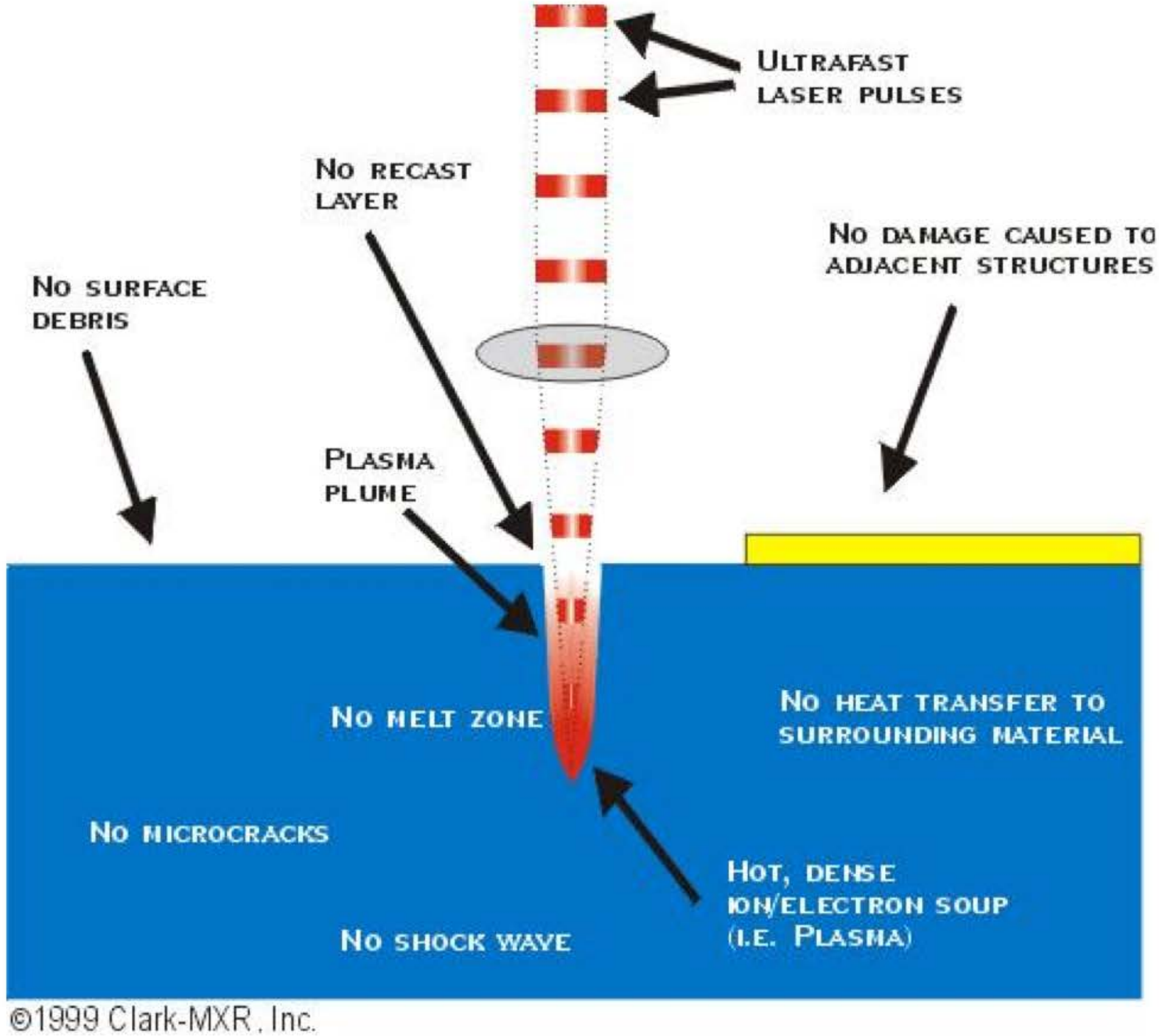
Laurin cell 2: Resonetics, Cetac

LFC, New Wave Research

New developements: ultrafast washout time : 30 ms! *Wang et al, anal. chem. 2013*

Supercell, New Wave Research

The femtosecond world…

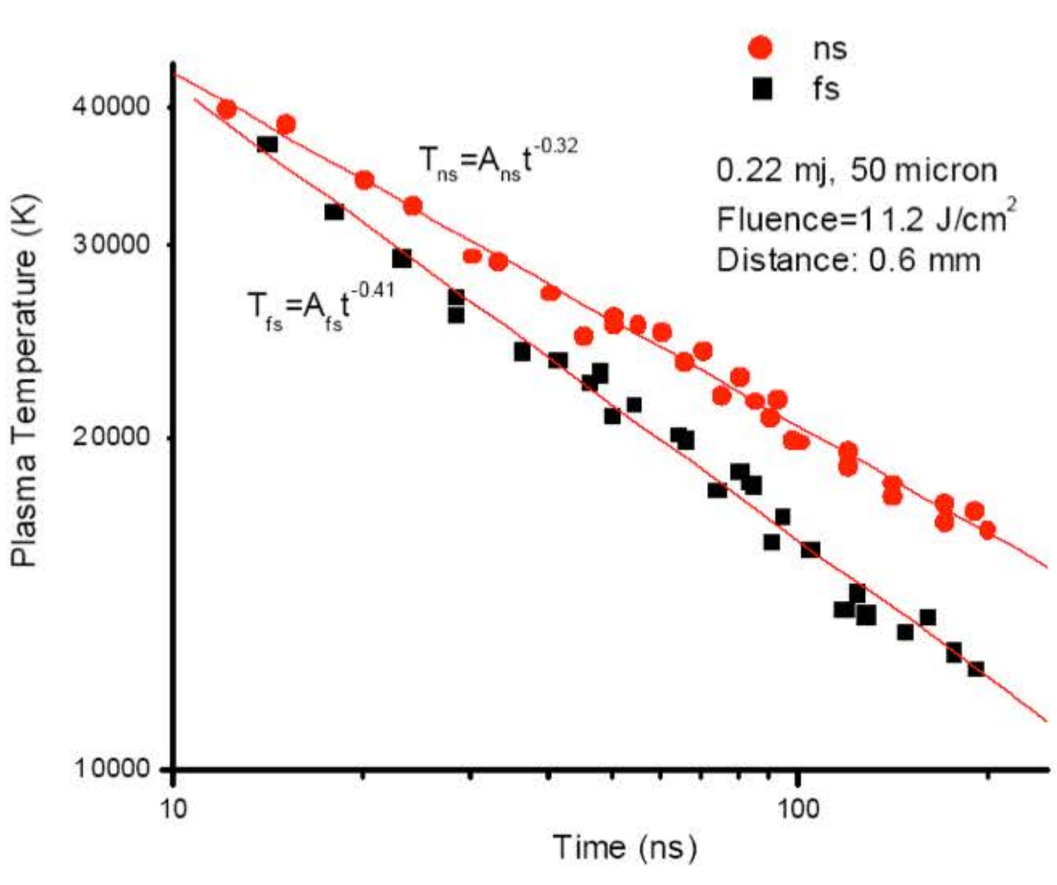


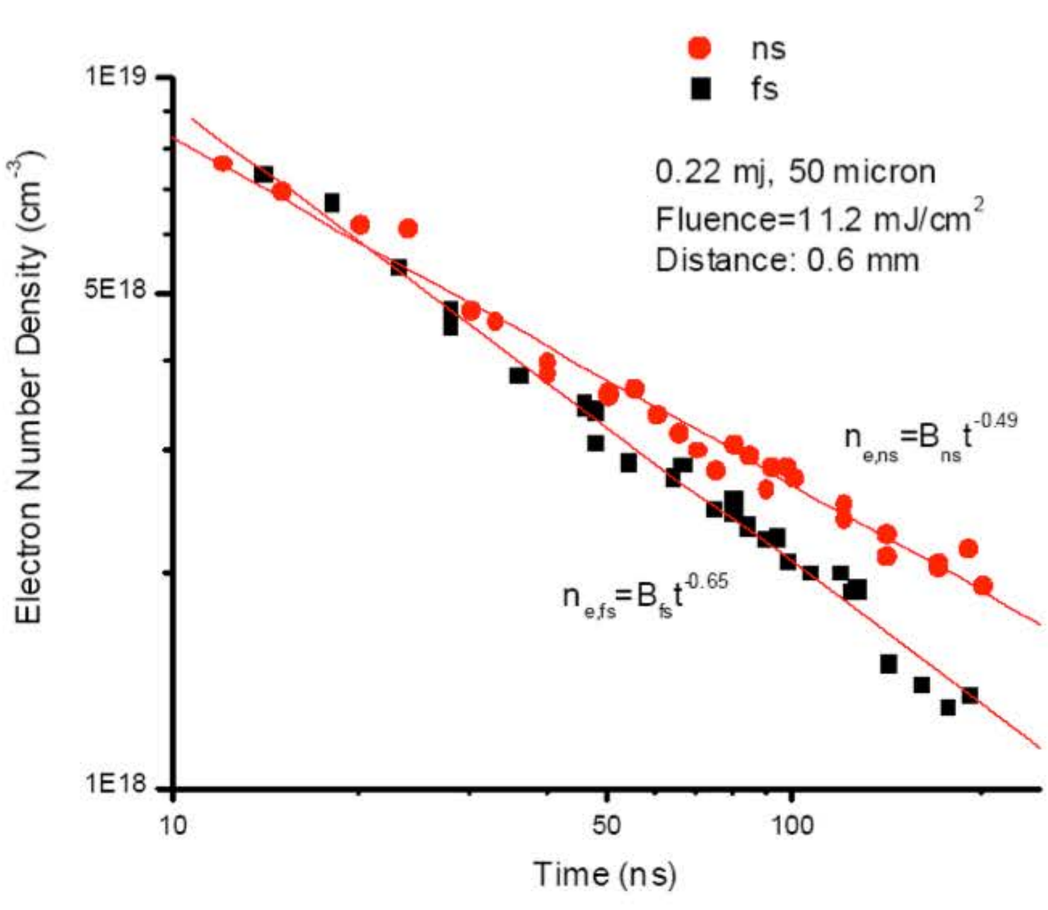
Ultra short pulses : femtosecond lasers

Nanosecond pulses:
Large heated zone
laser/plasma interaction
Large particle ejection due to melting

Femtosecond pulses:
The ablation process is confined in time and spatially
No laser/plasma interaction
Very thin particles are produced

Less thermal effects



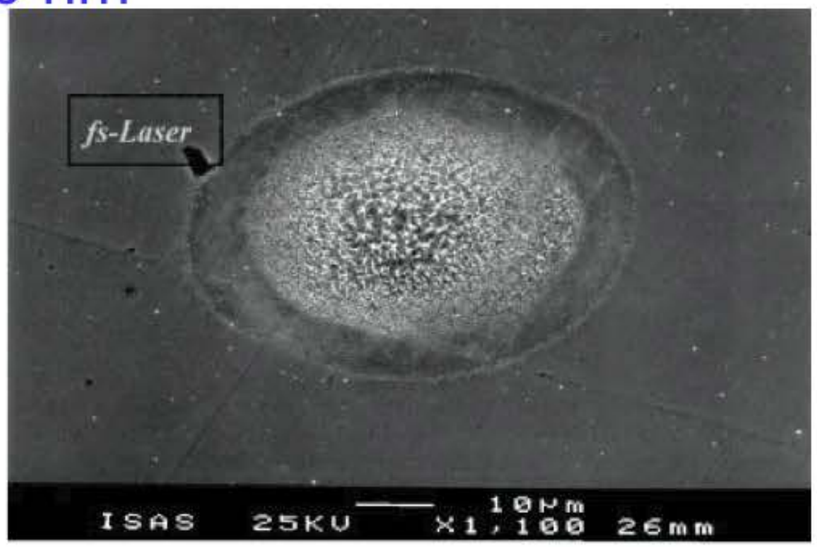


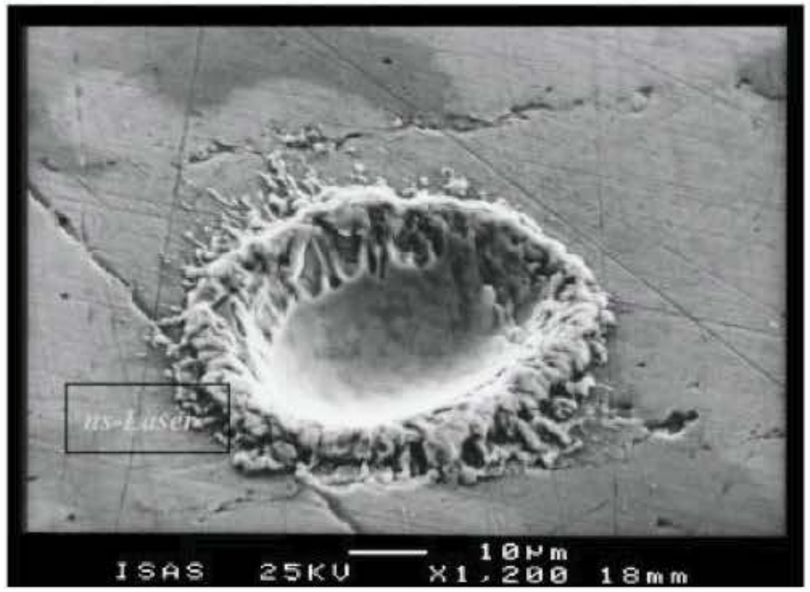
R. Russo – Winter conférence 2004

Short pulses versus ultra short pulses

Brass

Fs 800 nm





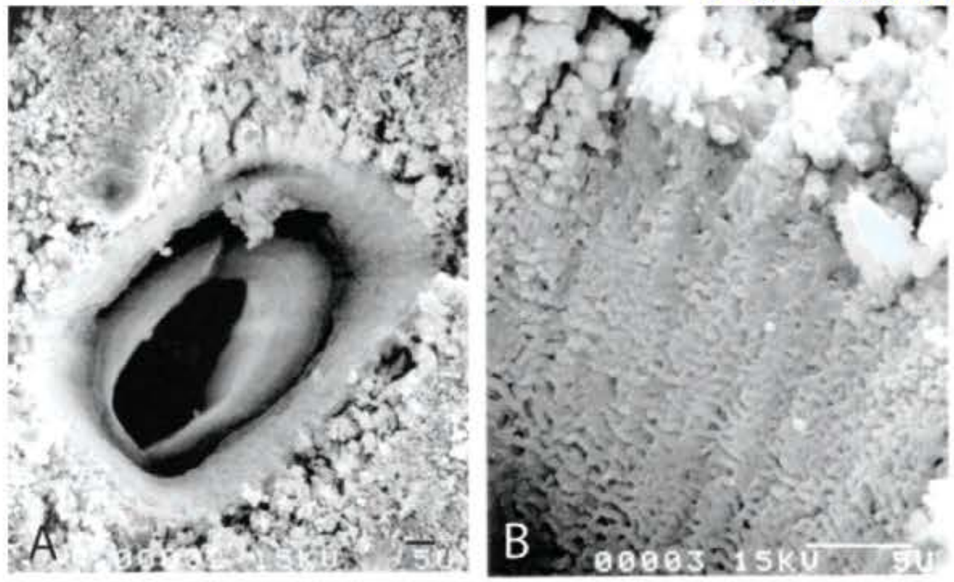
ns 800 nm

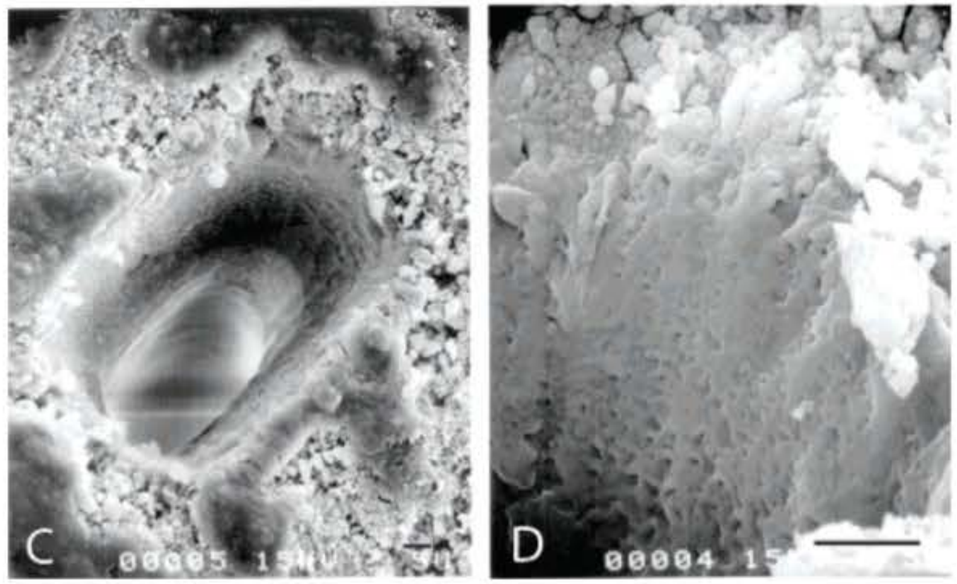
FIGURE 4. Fs- and ns-ablation of polished brass directly revealed different ablation mechanism. In both cases no beam shaping was used. Whereas the fs crater has a clean rim, the ns crater shows the typical pattern of melting. (Modified from Elsevier, Spectrochim. Acta B 55(2000)1771).

Hergenroeder et al, spectrochim. Acta B, 55,2000,1771

Glass

Fs 266 nm





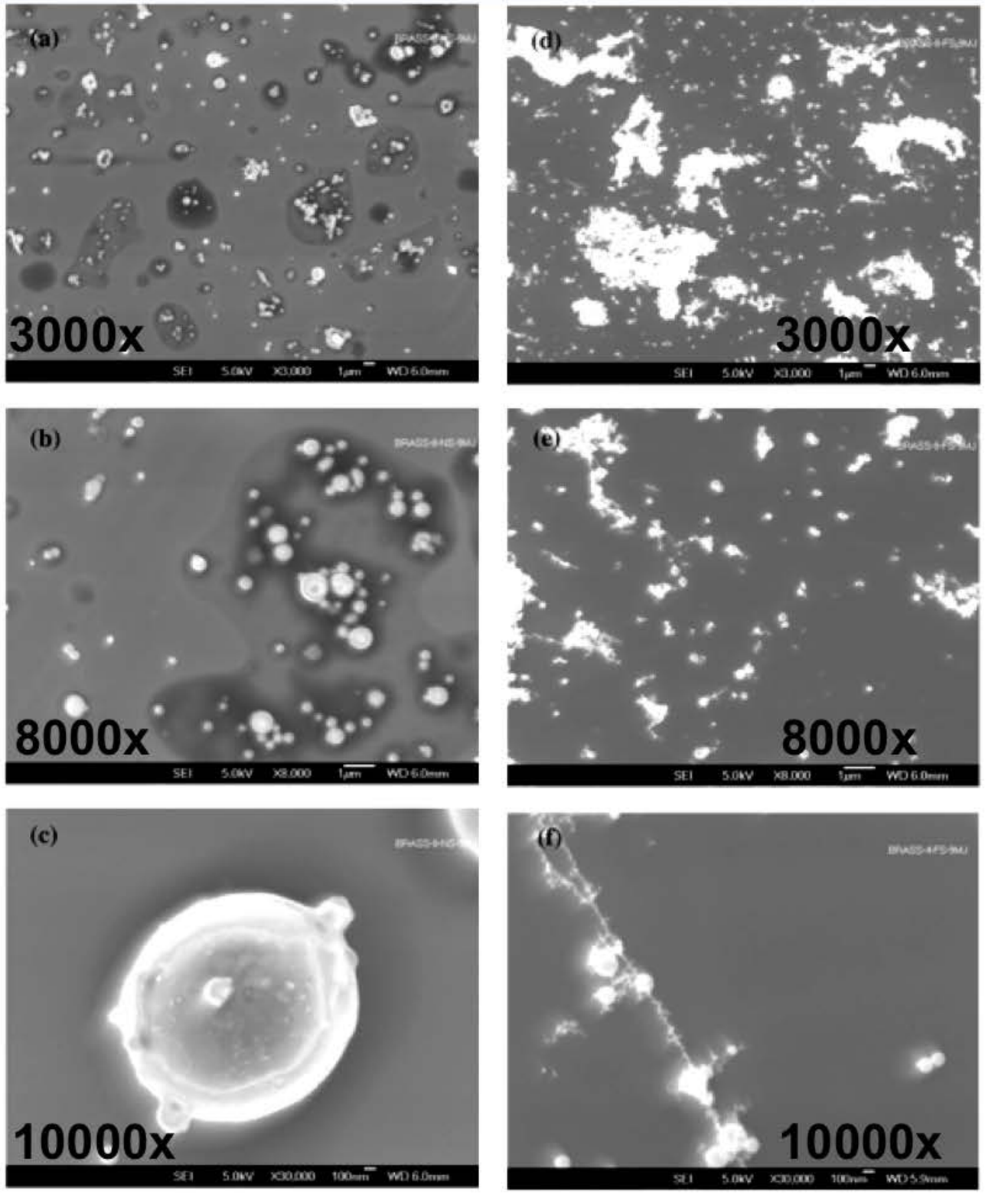
ns 266 nm

Poitrasson et al, Anal. Chem, 2003,75,6184-6190

Short pulses versus ultra short pulses

Brass

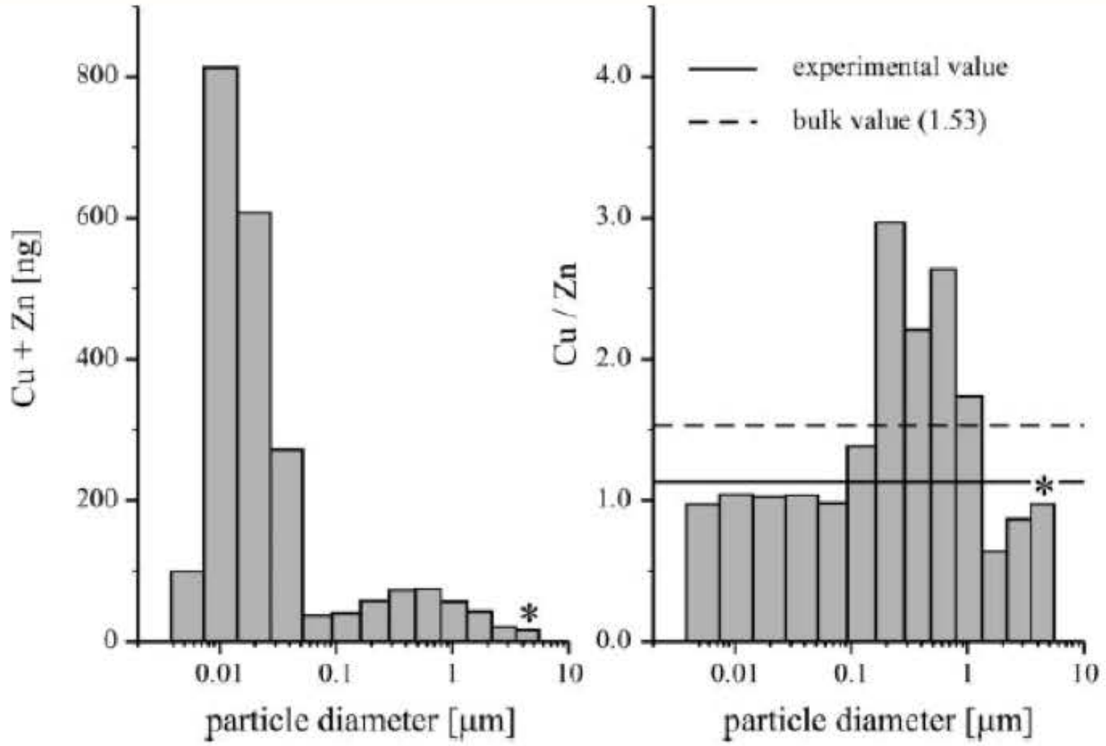
Nanosecond ablation 266 nm



Femtosecond ablation 266 nm

C.Liu et al, Anal. Chem. 76(2004) 1165

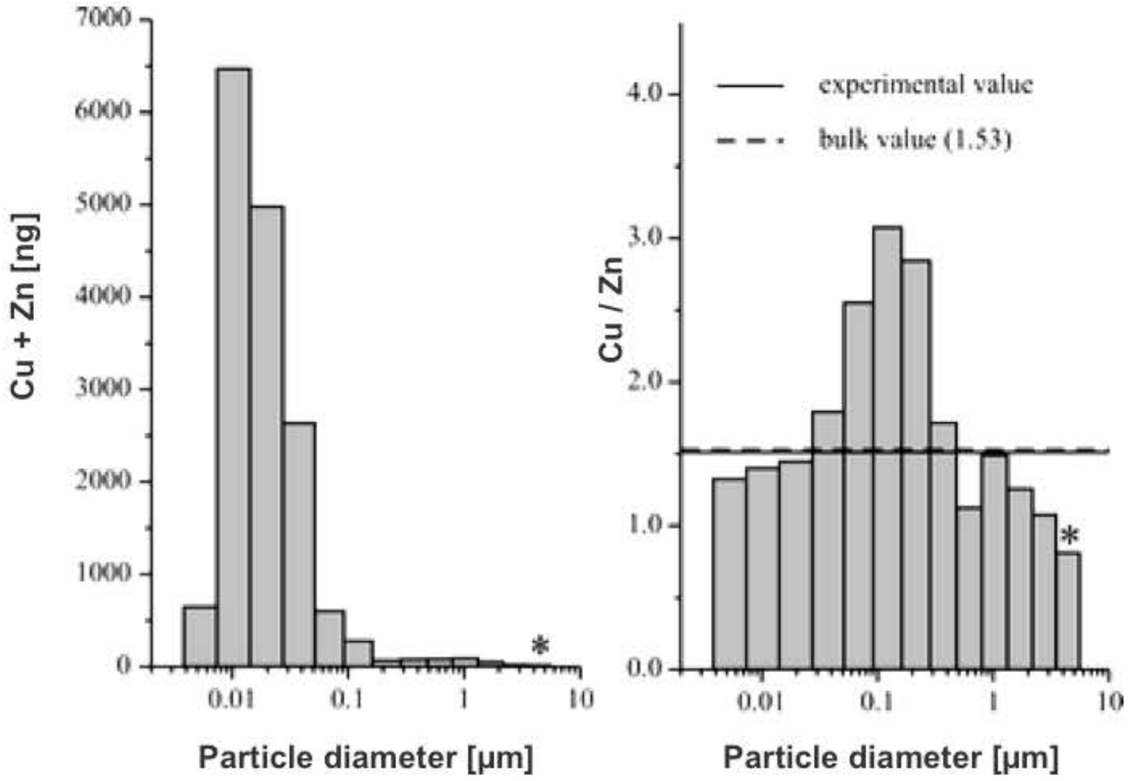
Short pulses versus ultra short pulses



Particle size distributions

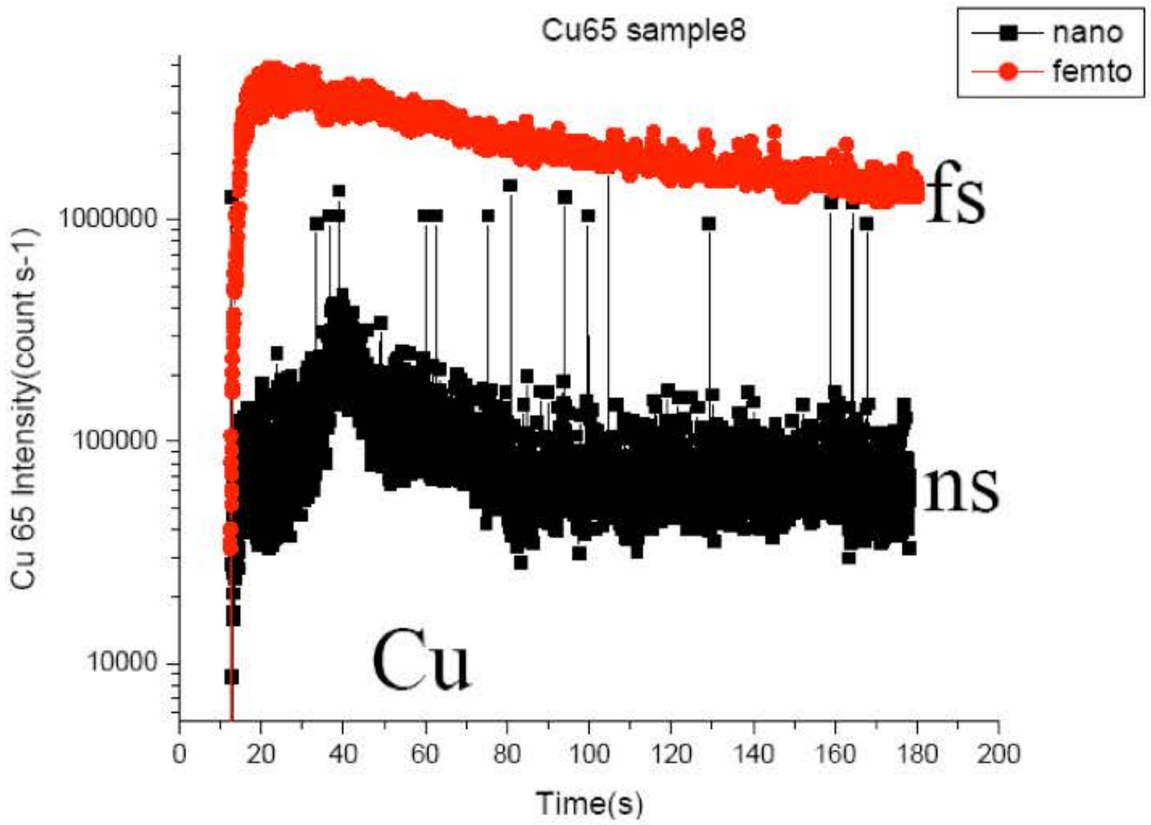
800 nm femtosecond LA
He, fluence 2.5 J.cm²

800 nm nanosecond LA
He, fluence 2.5 J.cm²



Koch et al, J . At. Spectrom., 2004, 19, 267–272

Short pulses versus ultra short pulses

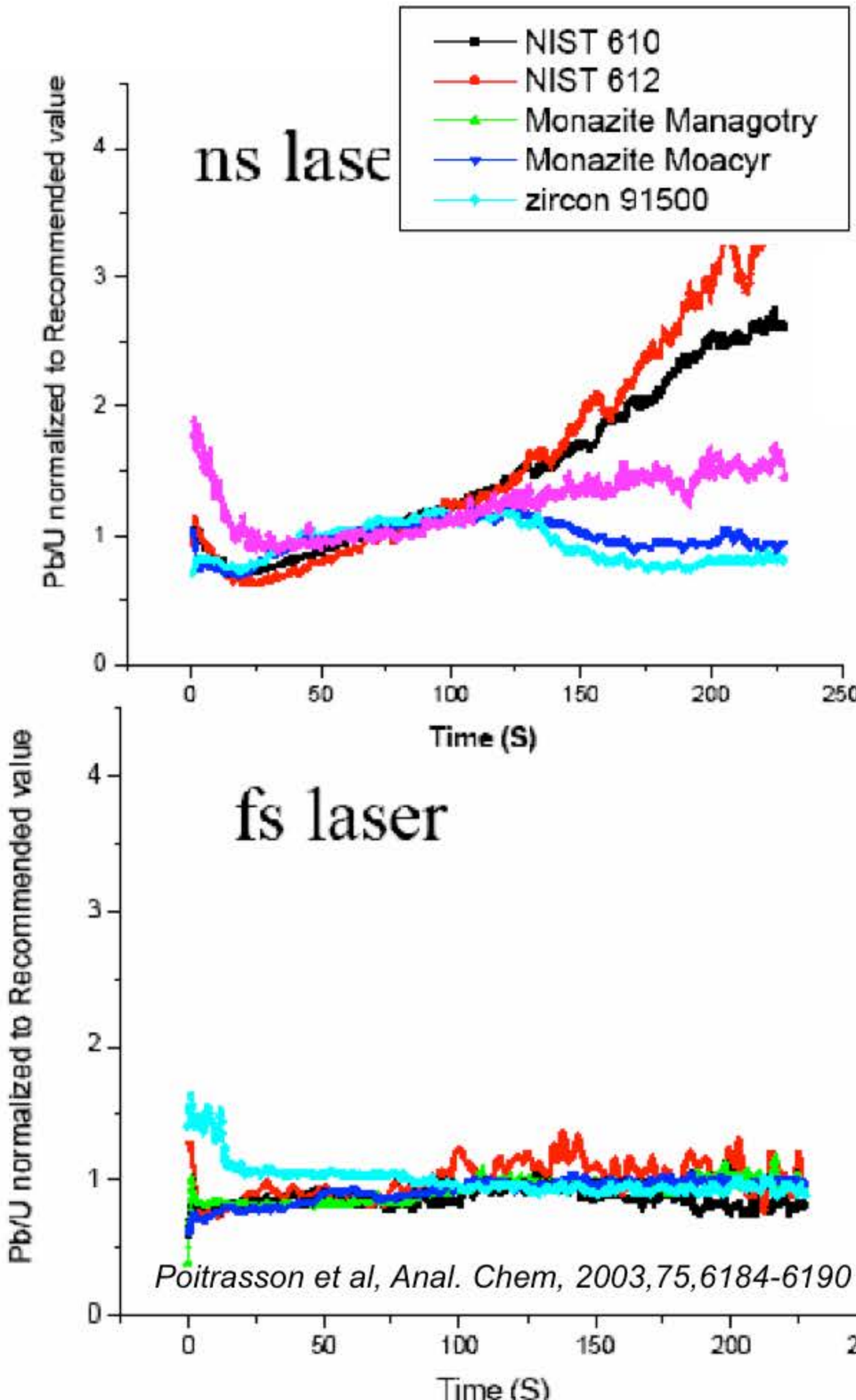


Very limited elemental fractionation due to:

- Very limited thermal effect (no preferential evaporation)
- production of thin particles easily atomised in the ICP
- Augmentation du signal d'un facteur 10

Stability improvement

Sensitivity improvement (mostly on metals)



Is non matrix match calibration possible?

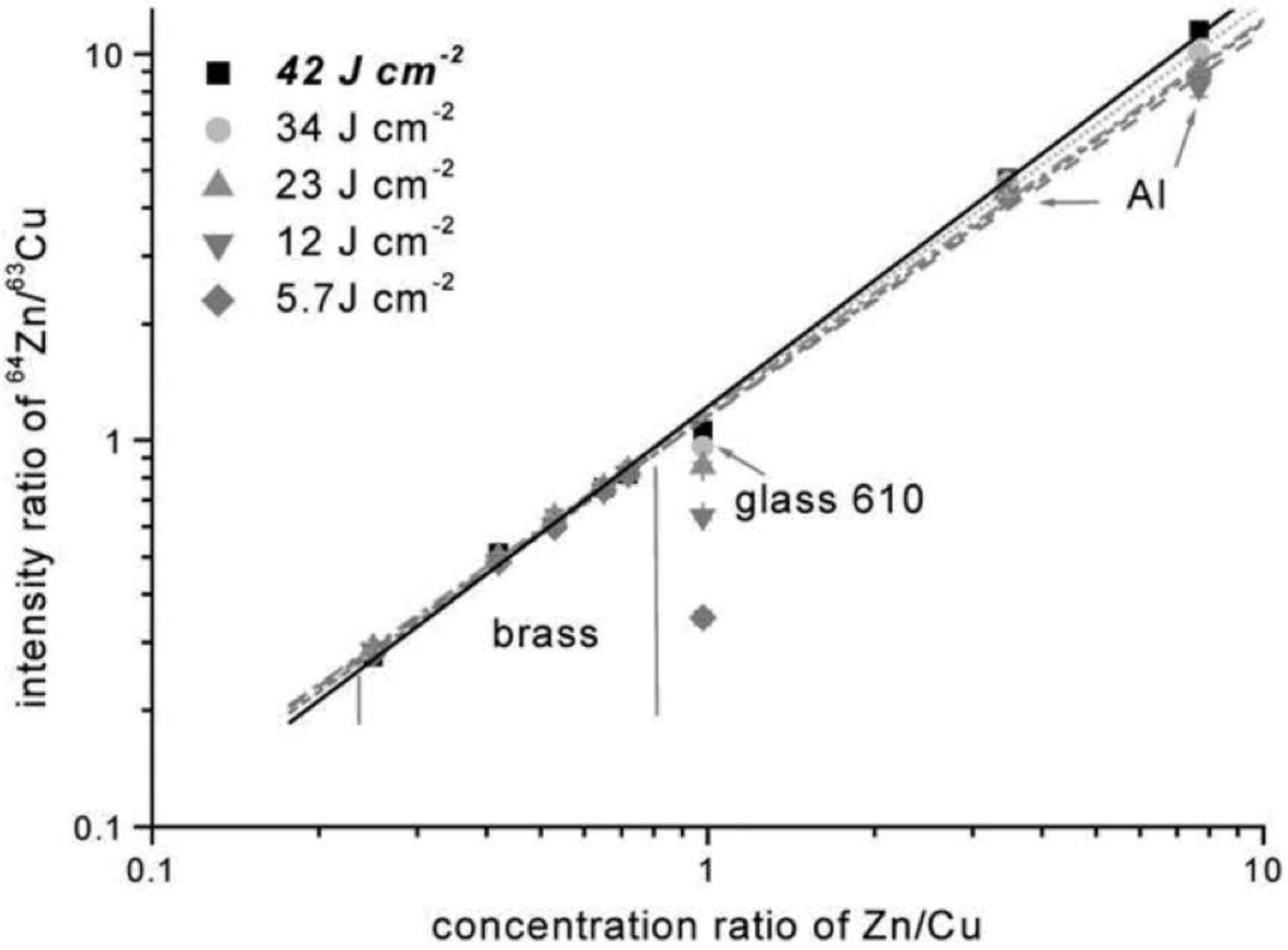


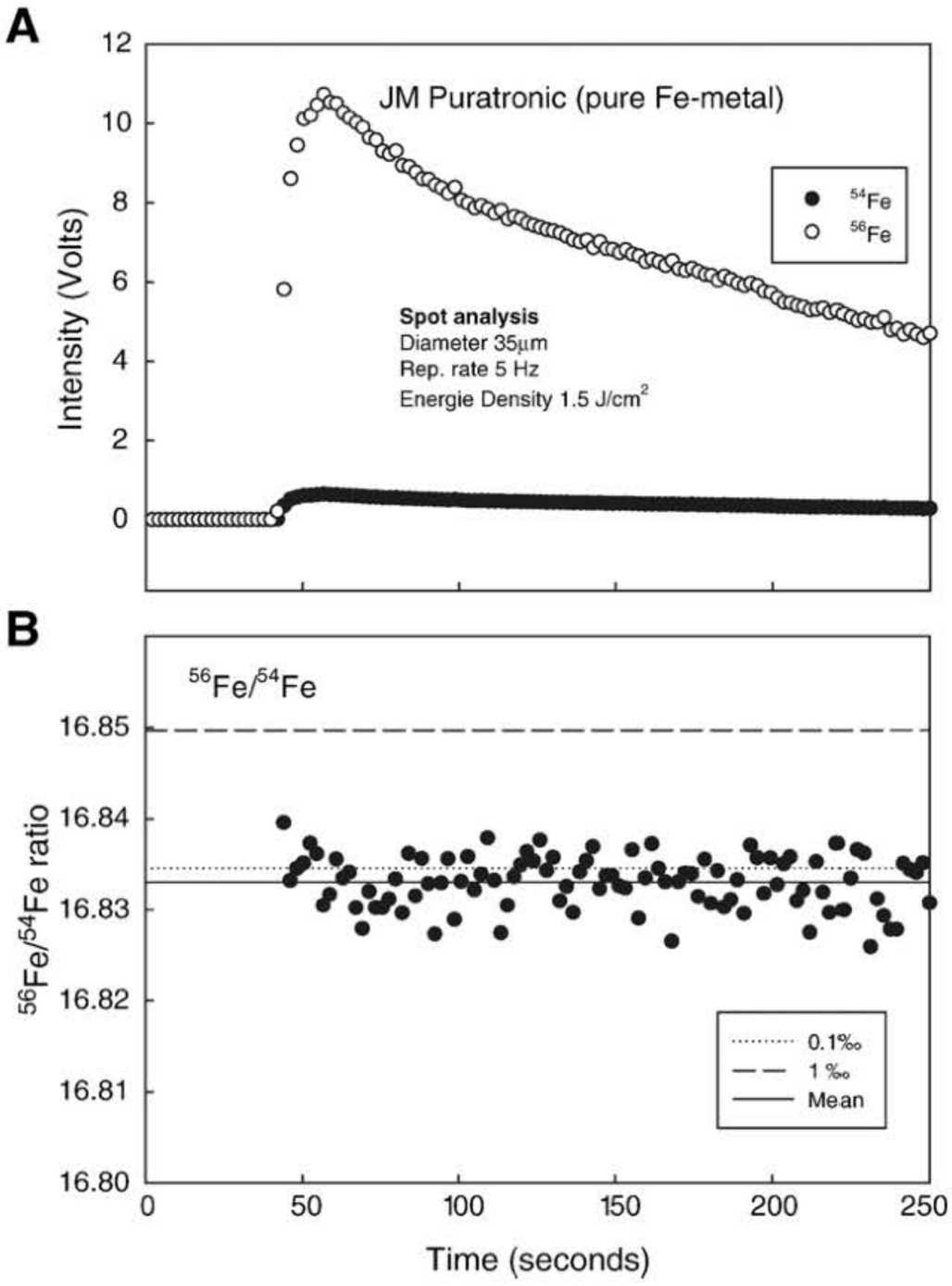
Fig. 3 The experimental 64Zn/63Cu ratio against the certified ratios for five brass, two aluminium and one glass sample measured with different fluences. The straight lines represent fits to the measured data (full line 42 J cm2; dotted line 34 J cm2; dashed-dotted line 23 J cm2; dashed line 12 J cm2; short dashed line 5.7 J cm2). The data for 42 J cm2 were recorded with a tighter focused beam while the fluence of the other measurements was varied by attenuation of the laser beam.

Q. Bian, JAAS, 2006,21,187-191

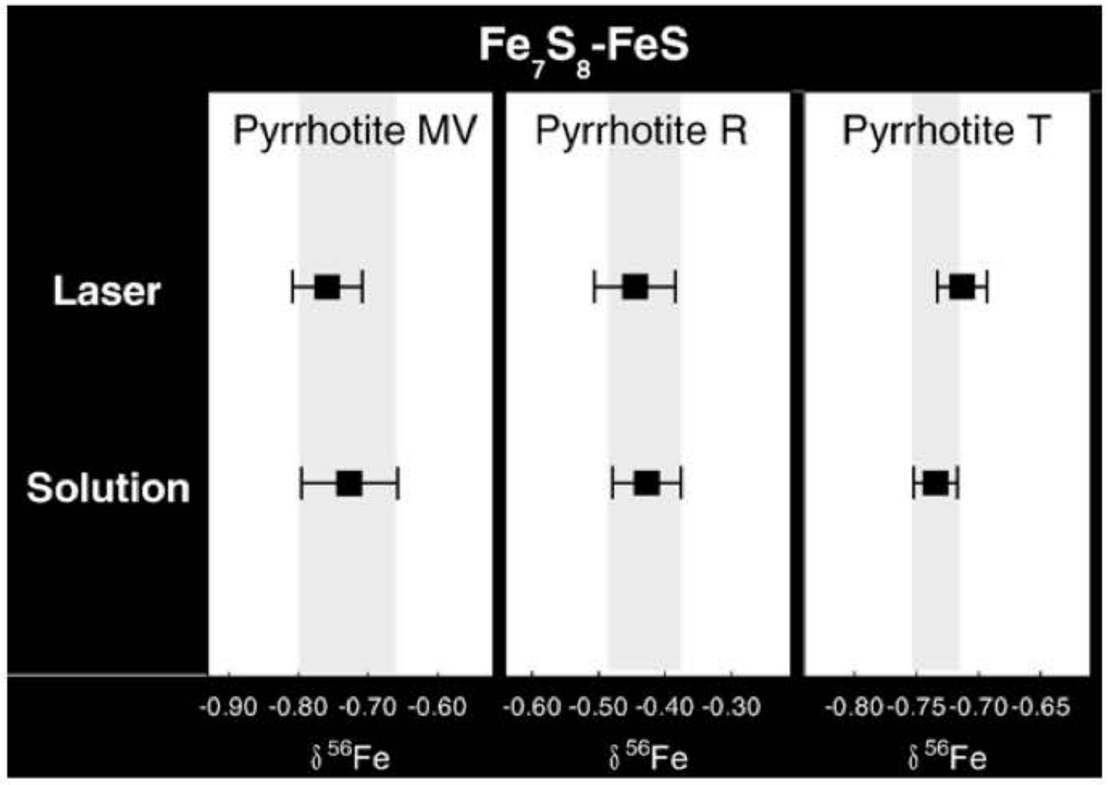
Non-matrix matched calibration

- High fluence for glass sample
- Low fluence for high thermal conductivity and low melting point sample (Al)

Isotopic fractionation?



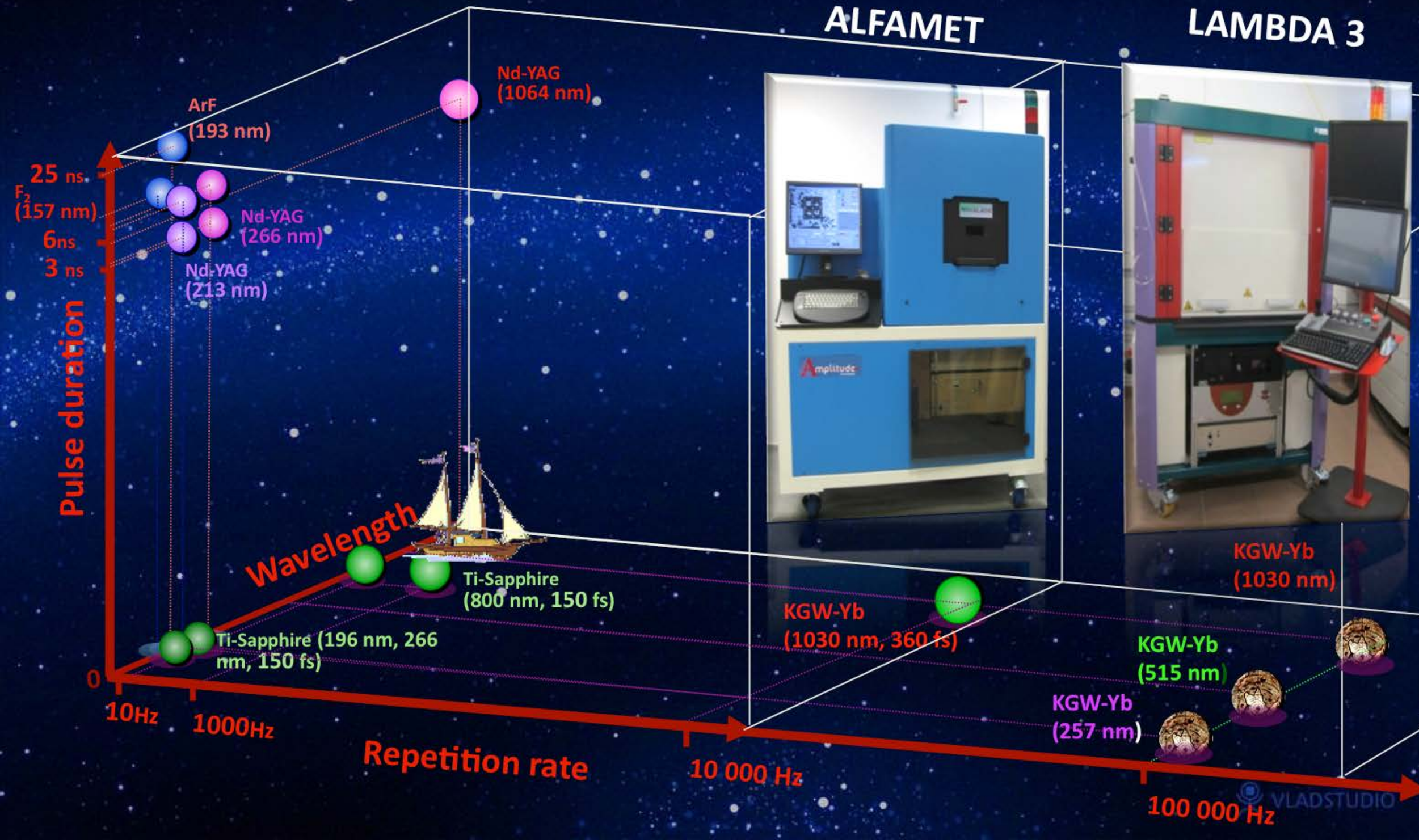
196 nm Fs LA/MCICPMS



No apparent isotopic fractionation

Horn et al, Spectrochimica Acta Part B 62 (2007) 410–422

More wavelenghts, higher repetition rate...



High repetition rate femtosecond laser…

s-Pulse oscillator/amplifier femtosecond laser

<10 kHz

E <O,1 mJ

- **Low energy (less than 2 mJ)**
- **High repetition rate (<100 kHz)**
- **pulse duration = 360 fs**
- **Crystal : KGW doped with Yb , 1030 nm in the fundamental**

<100 kHz

E < 2mJ

- **Diode pumped laser**
  - **Compact**
  - **Robust**

s-Pulse HP

Amplitude Systèmes, Pessac, France

First High repetition rate femto-ICPMS…

Alfamet : developed by LCABIE – Amplitude - Novalase

- **Fs pulses**
- **Compact**
- **Mobile**
- **Fully integrated**
- **Automated**
- **High spatial resolution**
- **Precise energie control**
- **High analytical performances**
- **Low energy**
- **High repetition rate**

First High repetition rate femto-ICPMS…

Low energy

high repetition rate
(10 KHz)

Fast laser beam movement

Crater size
5 - 30 µm

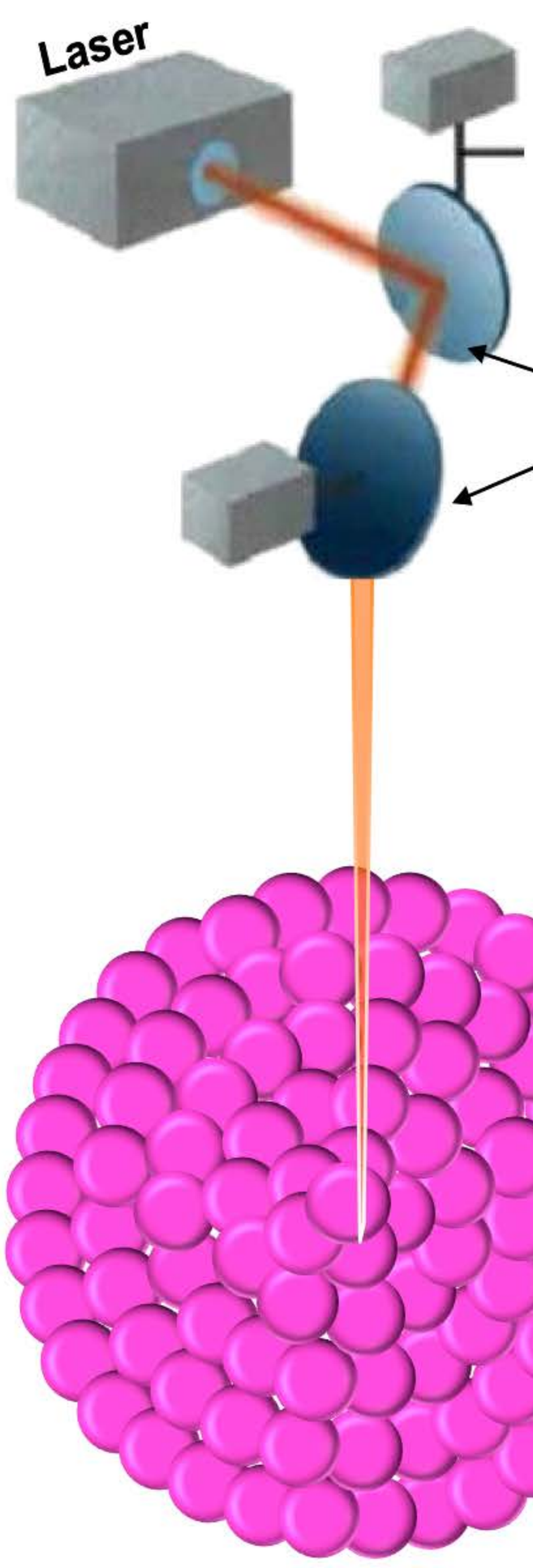
Surface analysis
High spatial res

Virtual beam shaping

Low sensitivity

Very High Analytical SENSITIVITY

Virtual beam shaping

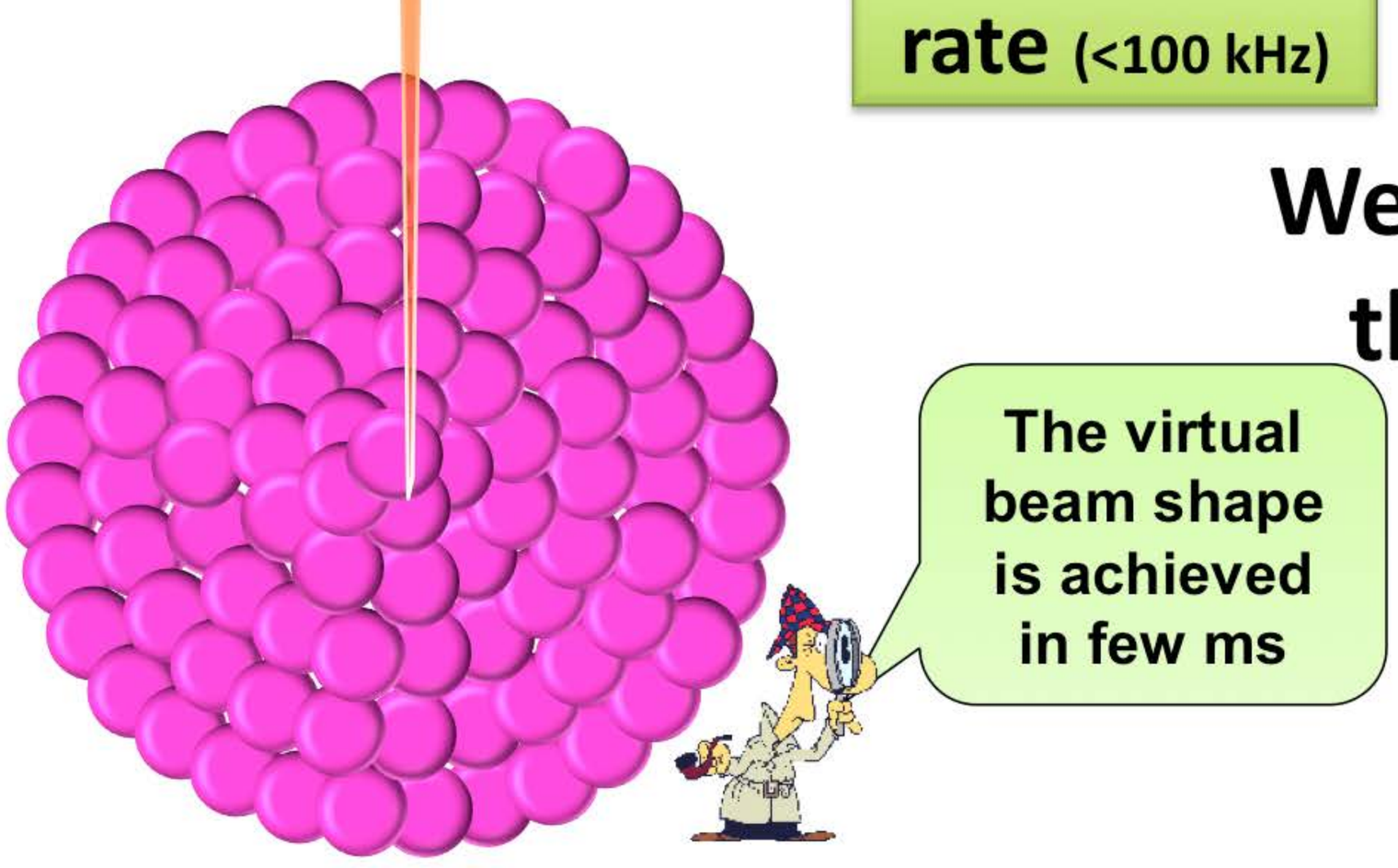


Small crater (≈ 10 µm)

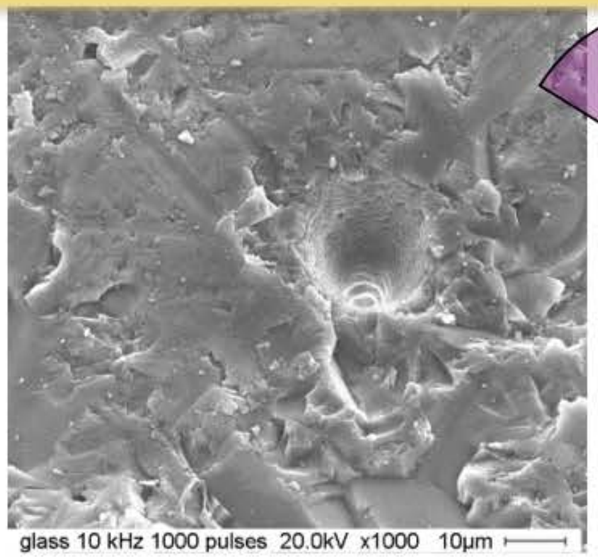
Fast beam scanning (<2 m/s)

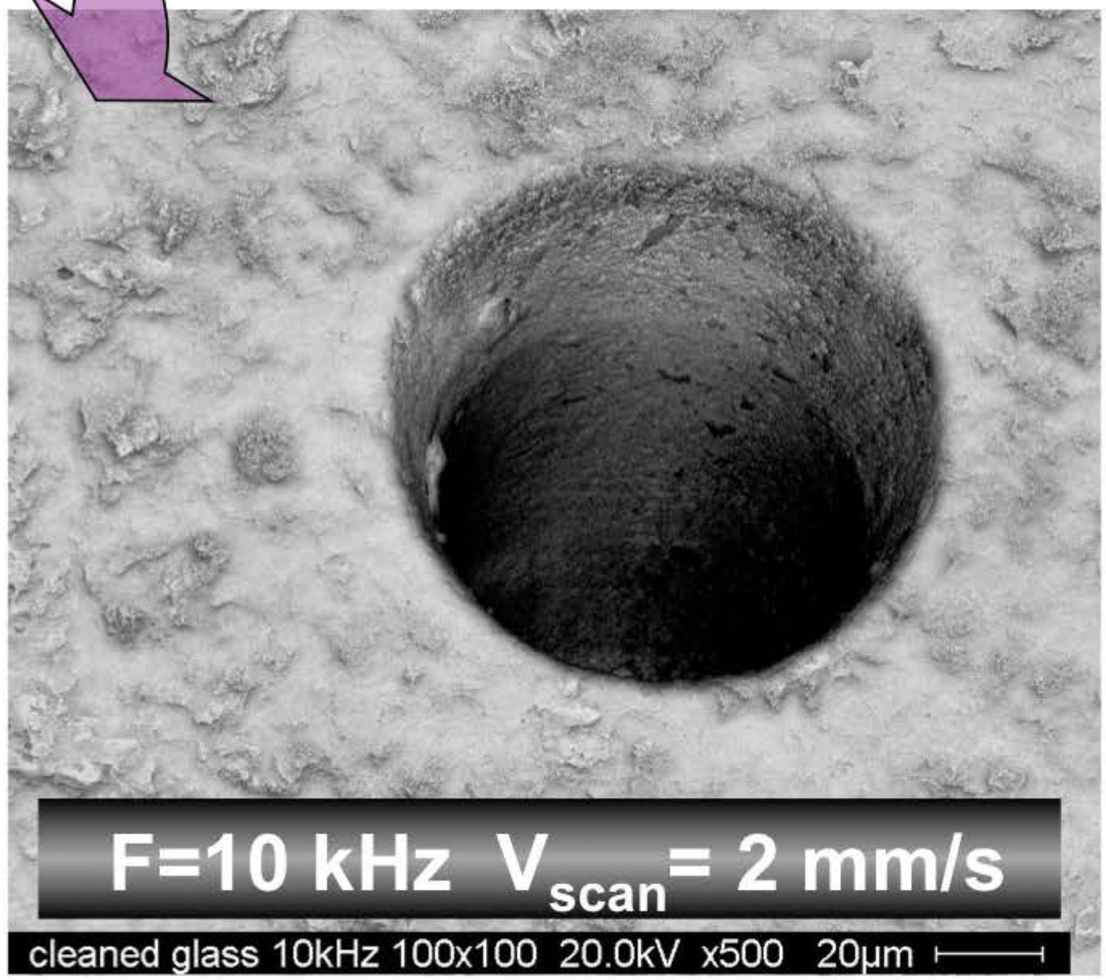
High repetition rate (<100 kHz)

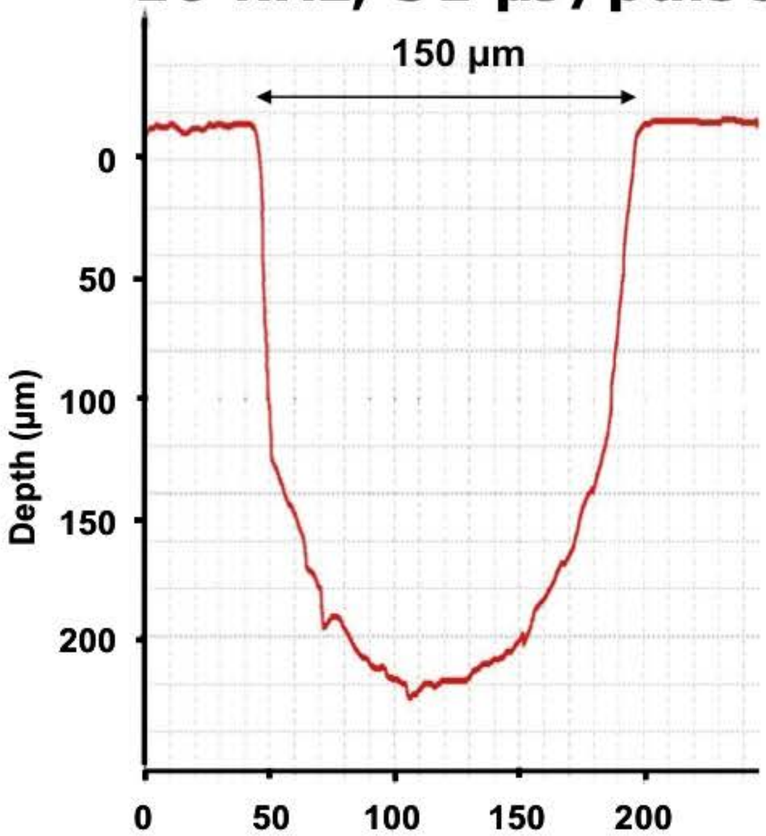
We can virtually adjust the apparent beam shape and size



Virtual beam shaping for flash ablation



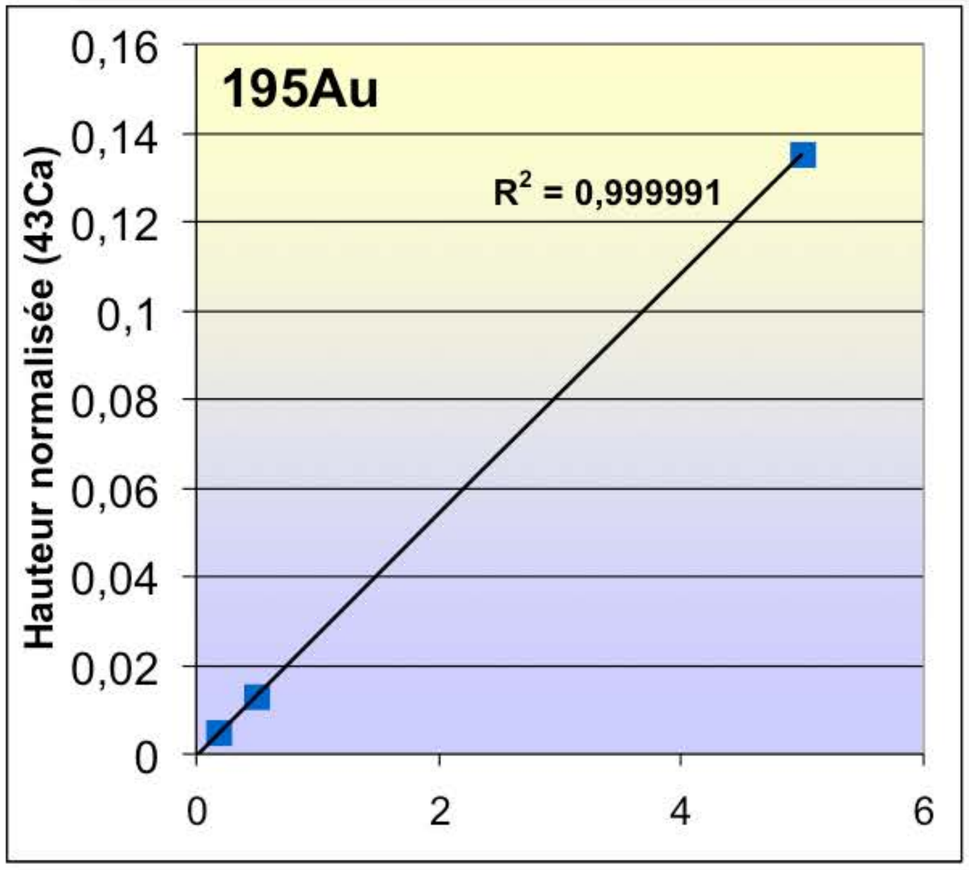


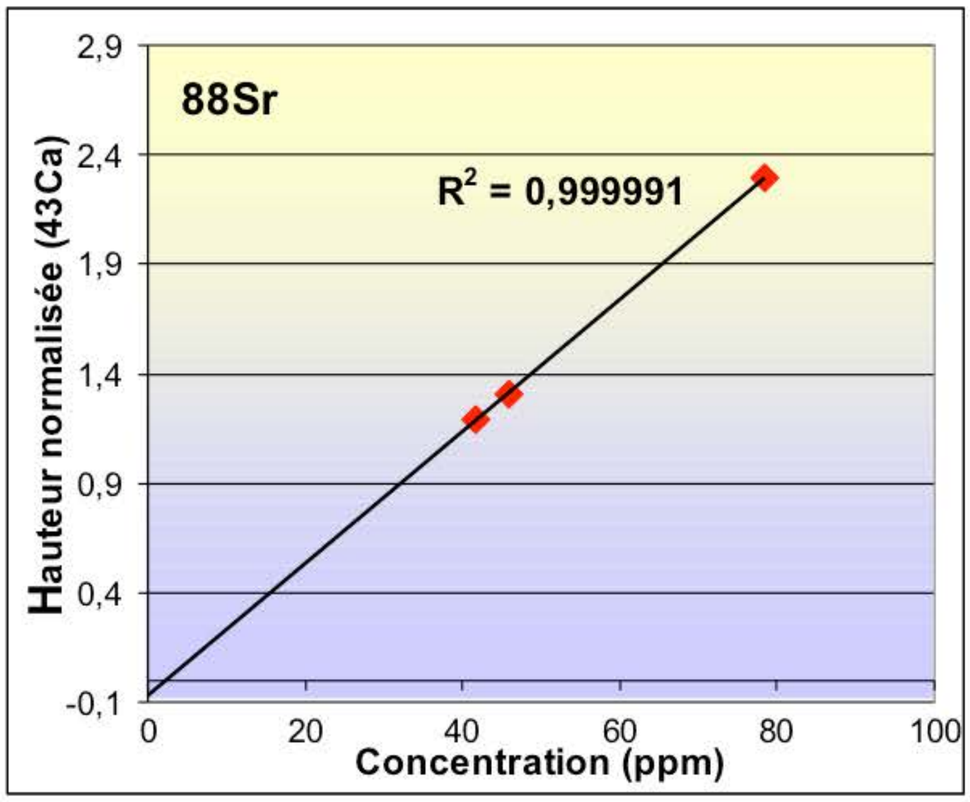


6 concentric circles
4710 craters in 0.47 s
Δx = 0.2 µm
Overlapping area = 99 %

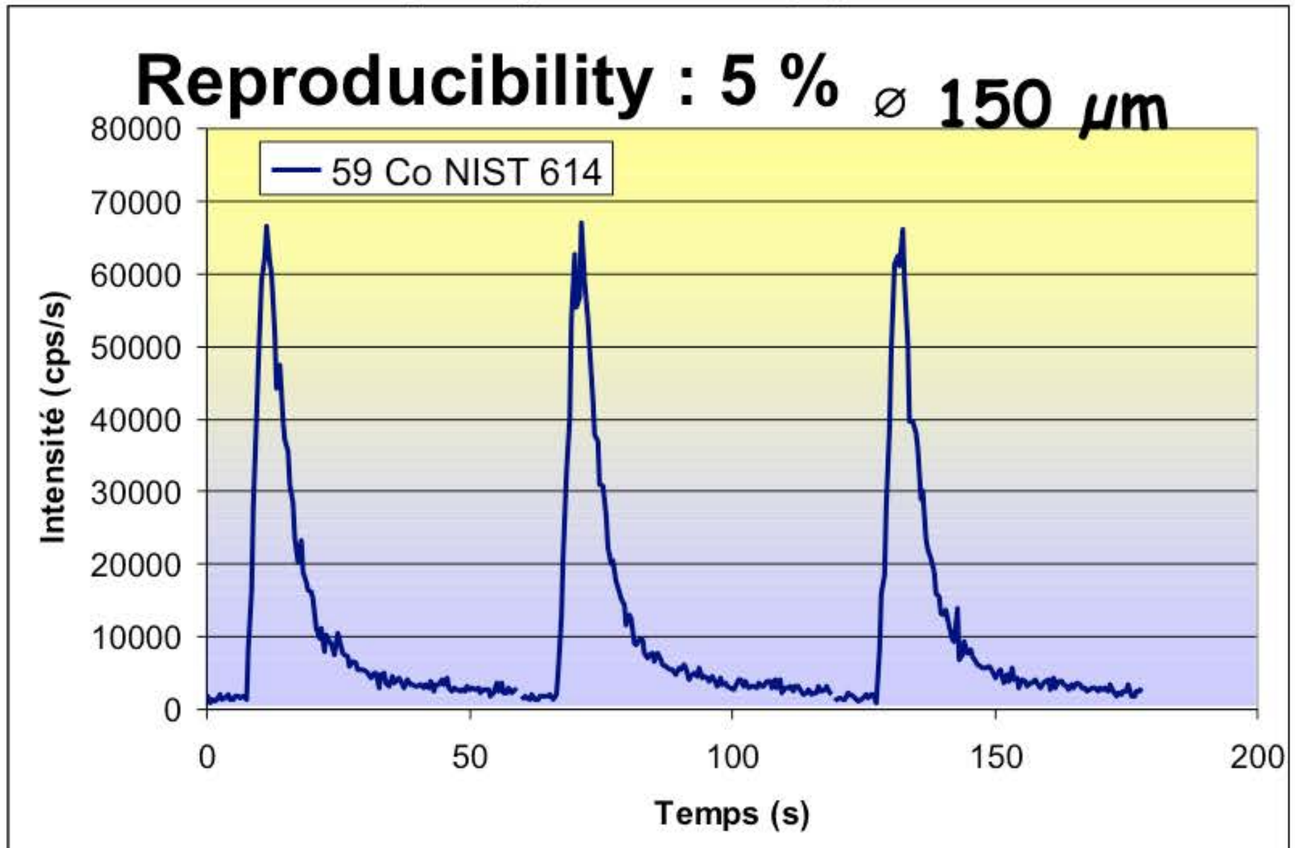
} X 100 times

Virtual beam shaping for flash ablation





Glass (NIST 614)
[Co] = 0,73 ppm



Max energy (here 0,5 uJ) @ 10 KHz

Virtual beam shaping for flash ablation : LOD

Using a Thermo X7 quad ICPMS

Femtosecond (360 fs) flash ablation

@ 150 µm

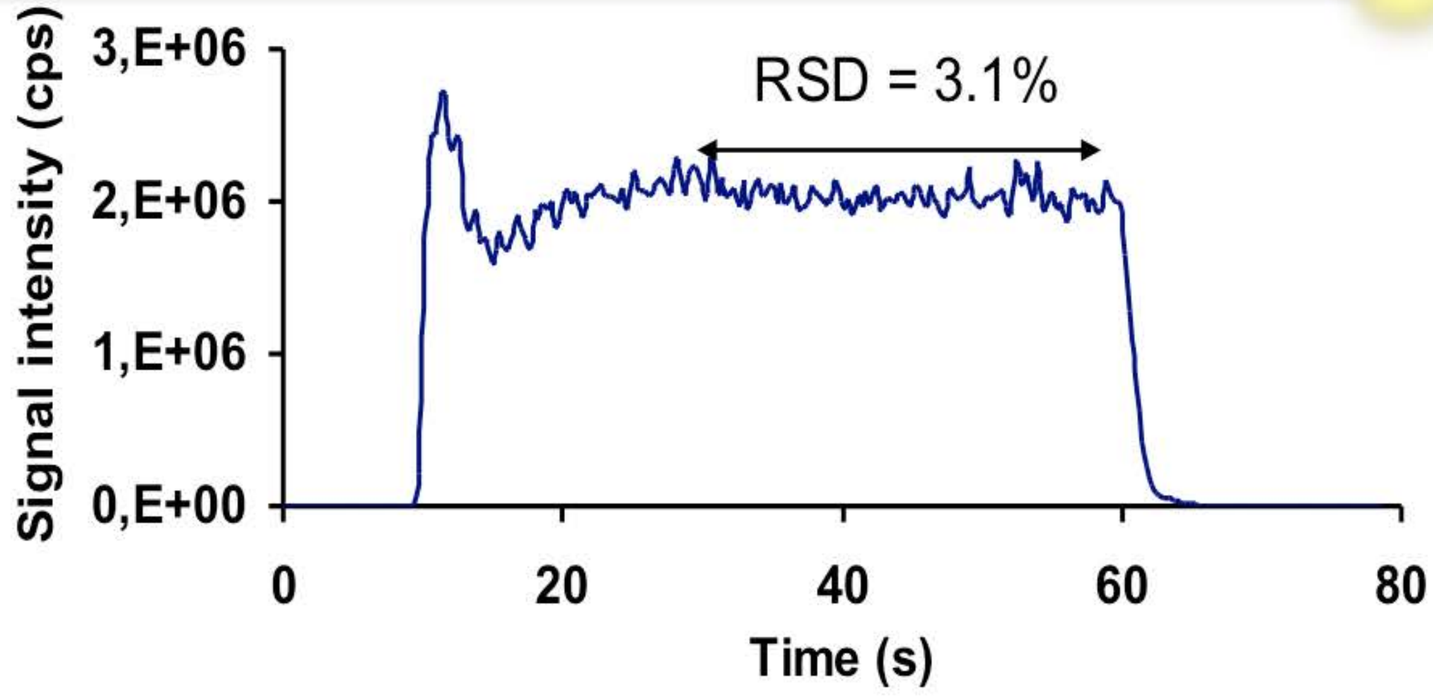
Nanosecond (8 ns) UV 266 nm, 20 Hz, 2mJ

Limites de détection (ng/g)	(nist 612) Femtoseconde	Improvement factor compared to 266 nm ns laser
^{59}Co	14,1	x 25
^{65}Cu	38,6	x 12
^{88}Sr	3,3	x 26
^{107}Ag	1,10	x 8
^{111}Cd	7,83	
^{197}Au	0,73	x 10
^{205}Tl	0,42	x 13
^{208}Pb	1,10	x 11
^{232}Th	0,15	x 41
^{238}U	0,13	x 16

Signal stability

Femtosecond IR 1030 nm

Energy : 75 µJ/pulse
Repetition rate : 500 Hz
Ablated width : 100 µm;
Stage speed: 10 µm/s

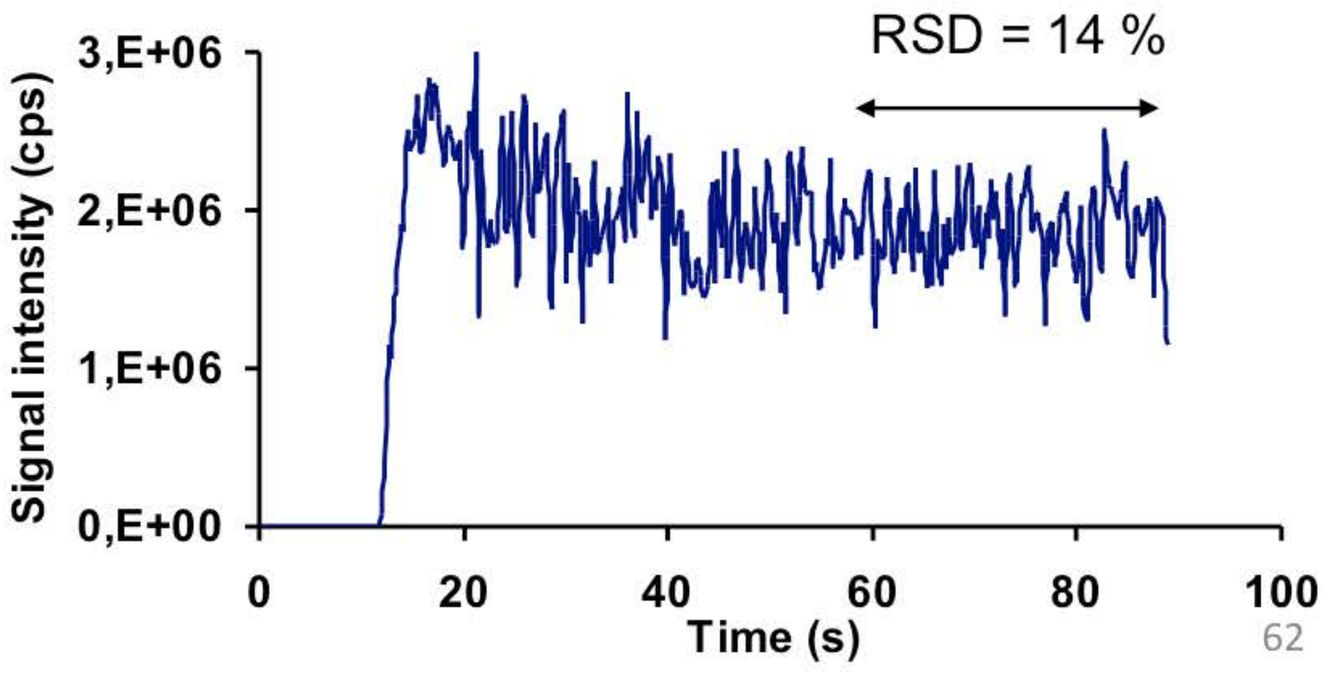


Single line scanning ablation mode

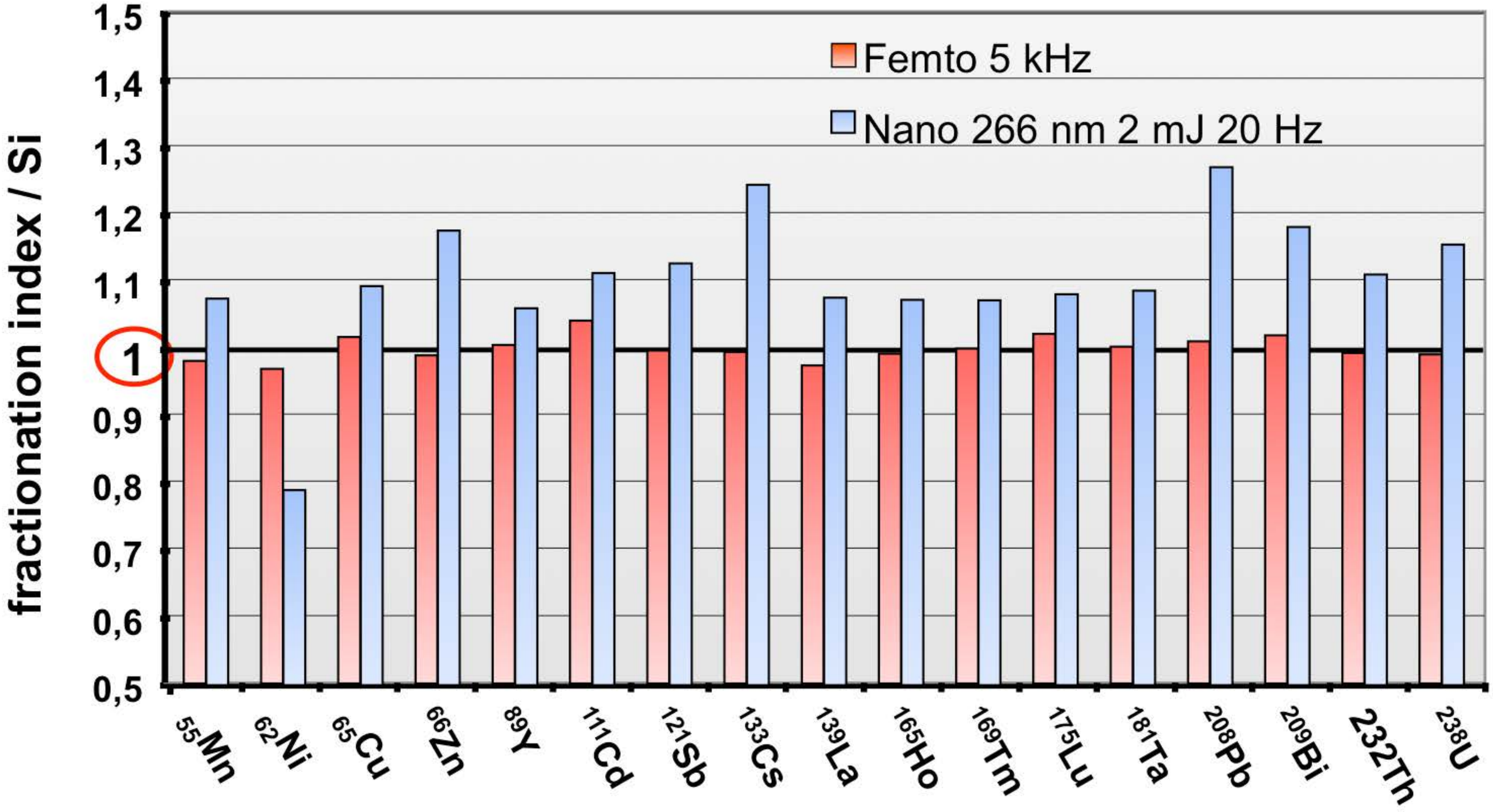
Ablation of a certified glass sample (NIST 612) Indium

Nanosecond UV 266 nm

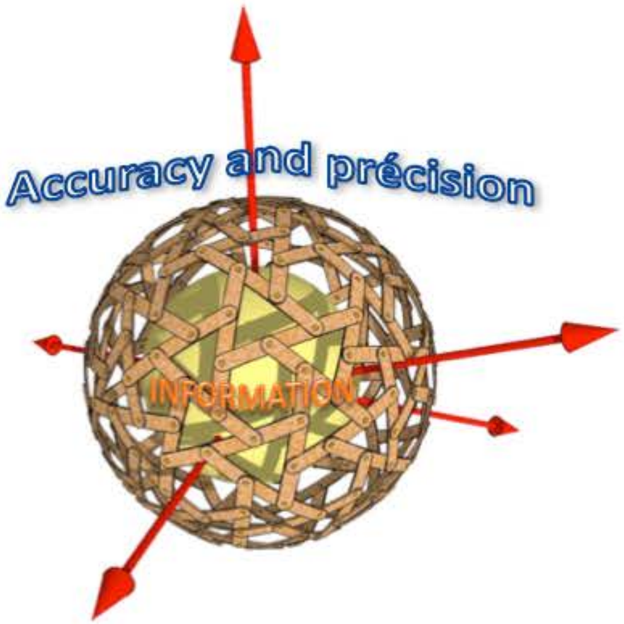
Energy : 1.3 mJ µJ/pulse
Repetition rate :20 Hz
Ablated width : 100 µm;
Stage speed: 10 µm/s



Elemental fractionation



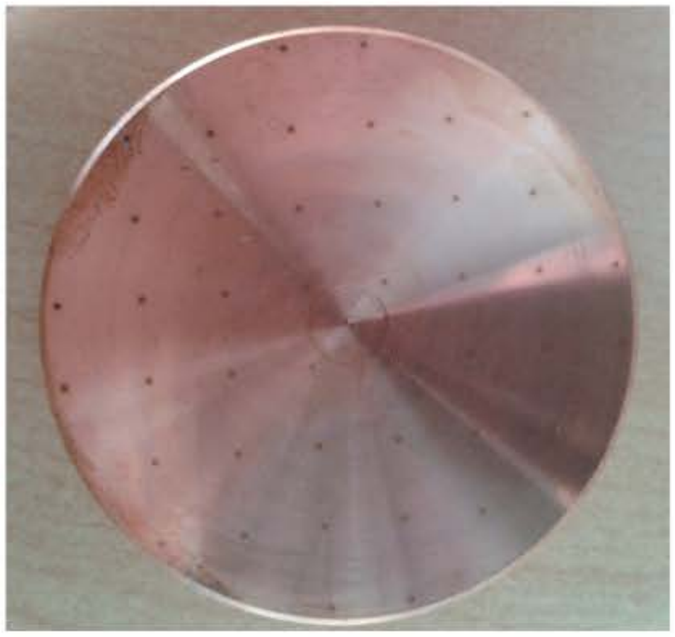
Elemental fractionation



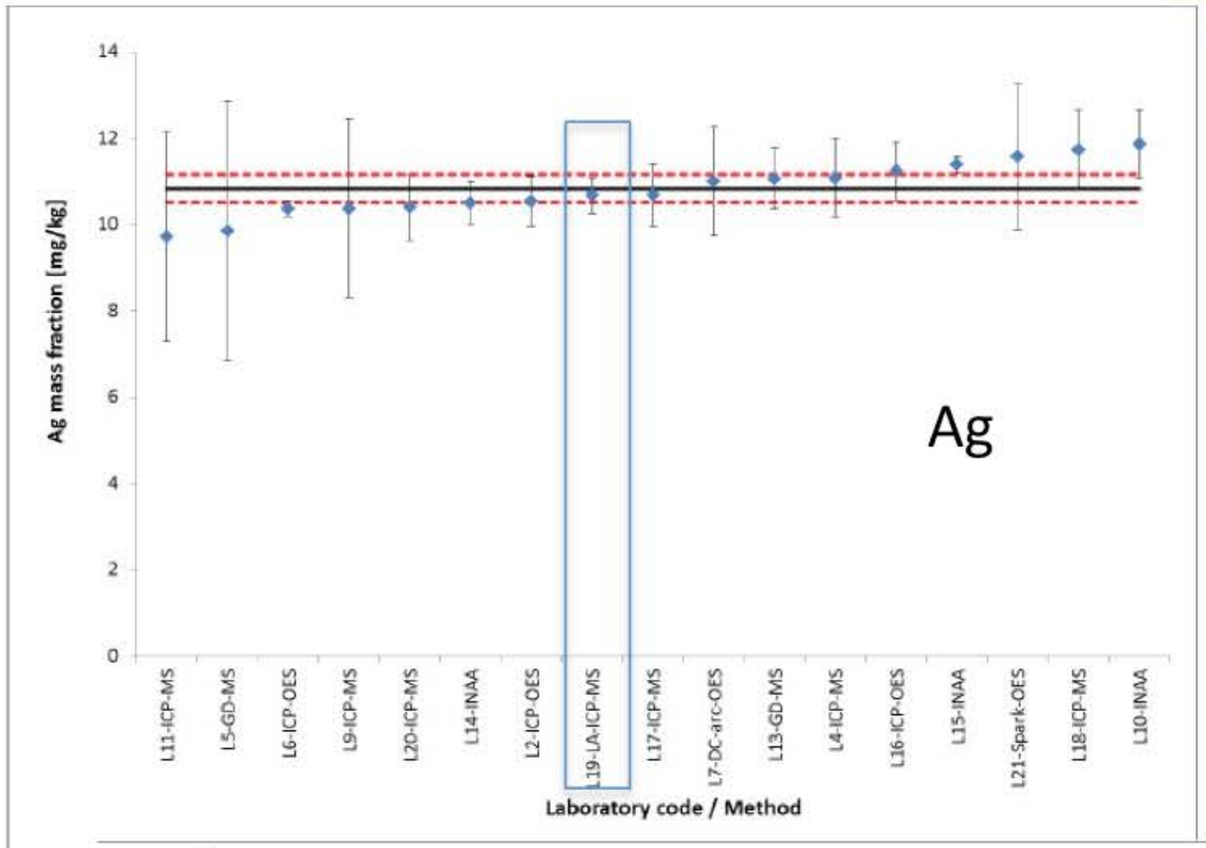
The intrinsec properties of fs pulses are preserved even at high repetition rate ...

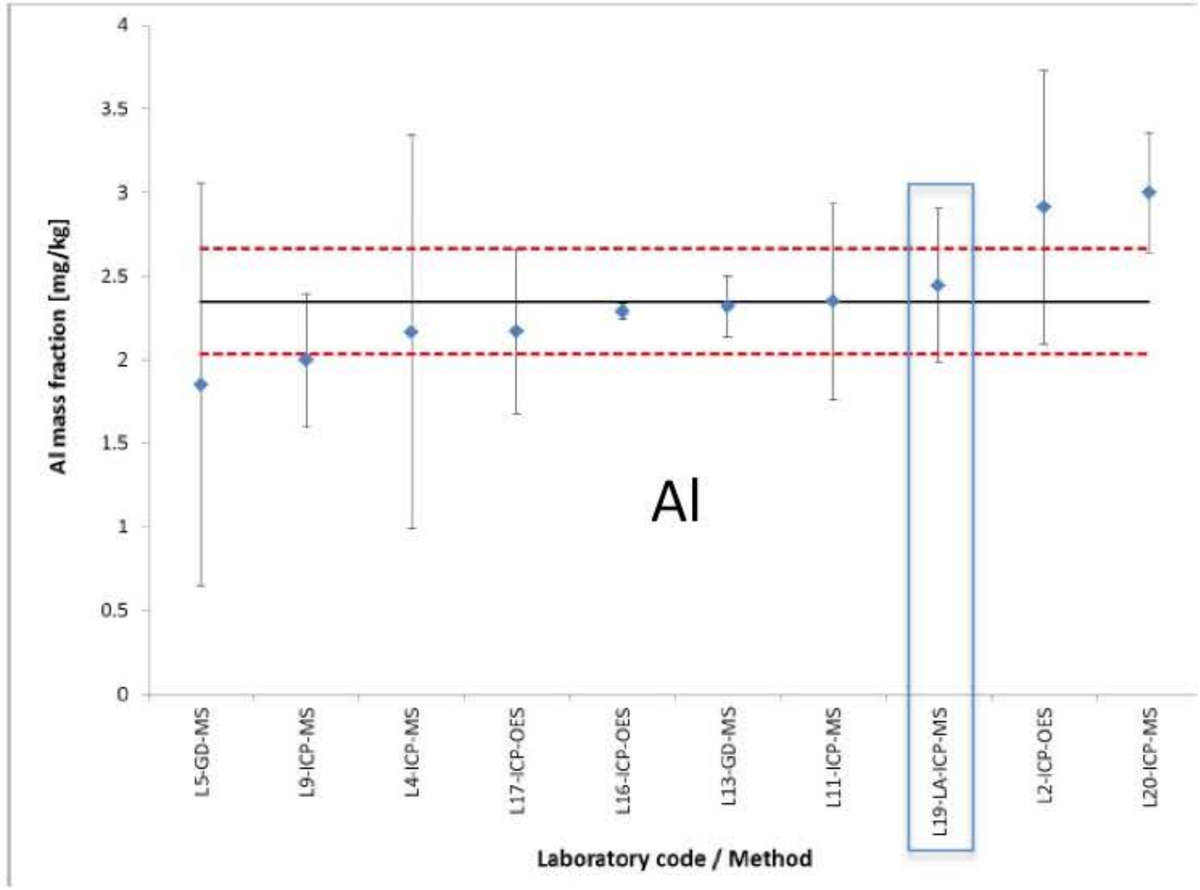
JAAS, 24 (7), 2009, pp. 891-902

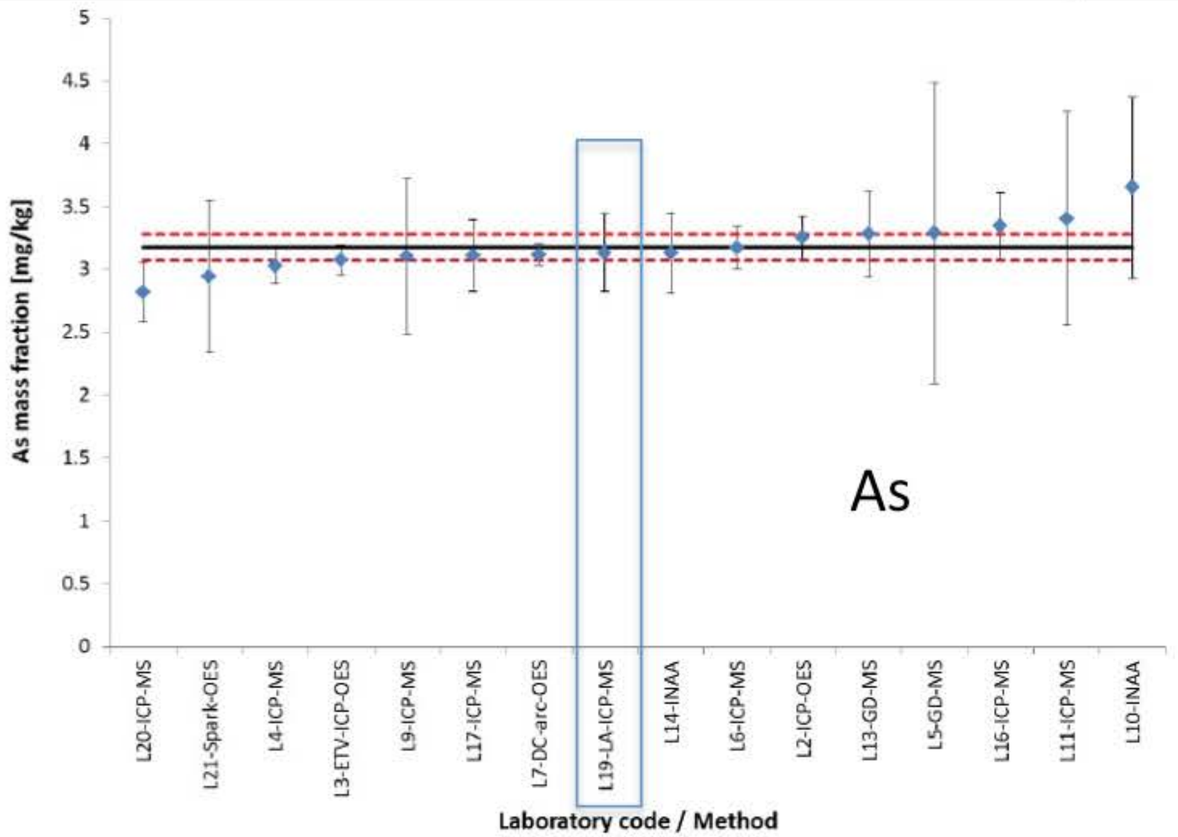
Trace elements in copper – Round Robin



ICPMS
ETV-ICPOES
GDMS
ICPMS
ICPAES
SPARK OES
etc...
and fsLA-ICPMS



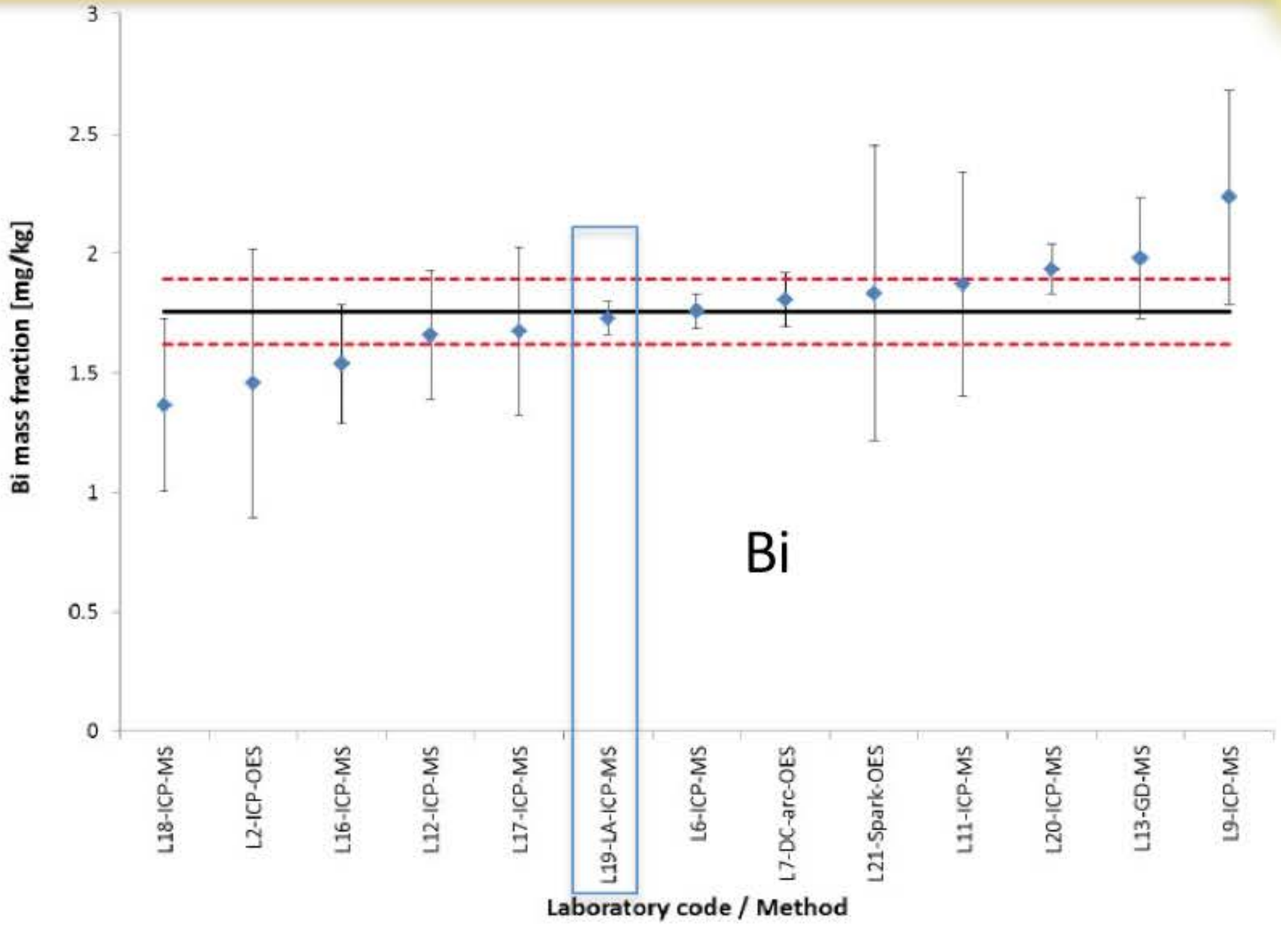


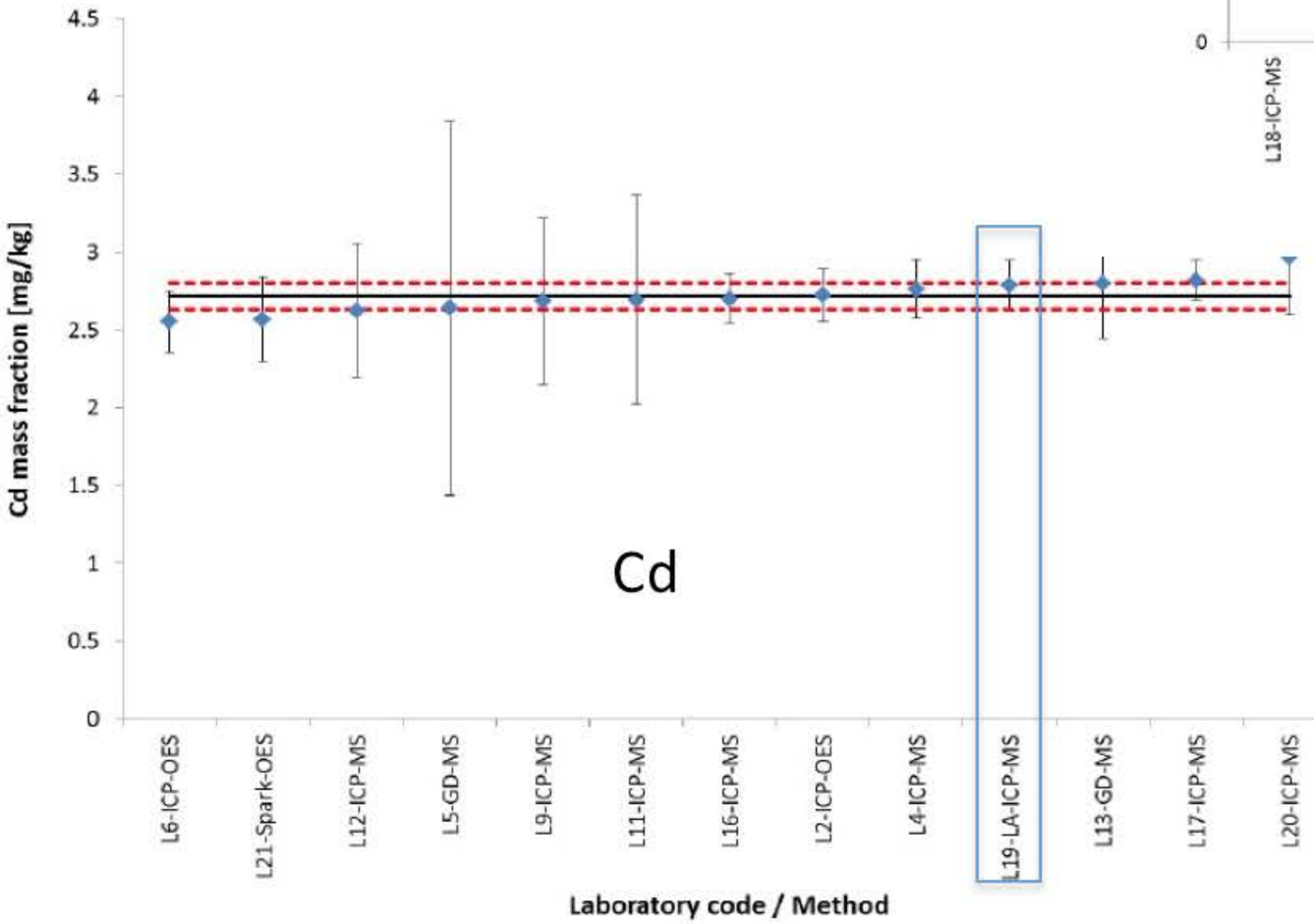


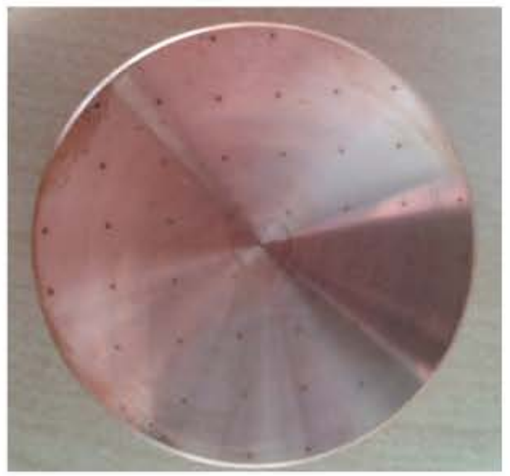
Trace elements in copper – Round Robin

Femtosecond laser ablation provides good precision and accuracy.

Note that due to the high thermal conductivity of Cu, laser ablation is not a priori the best indicated approach.



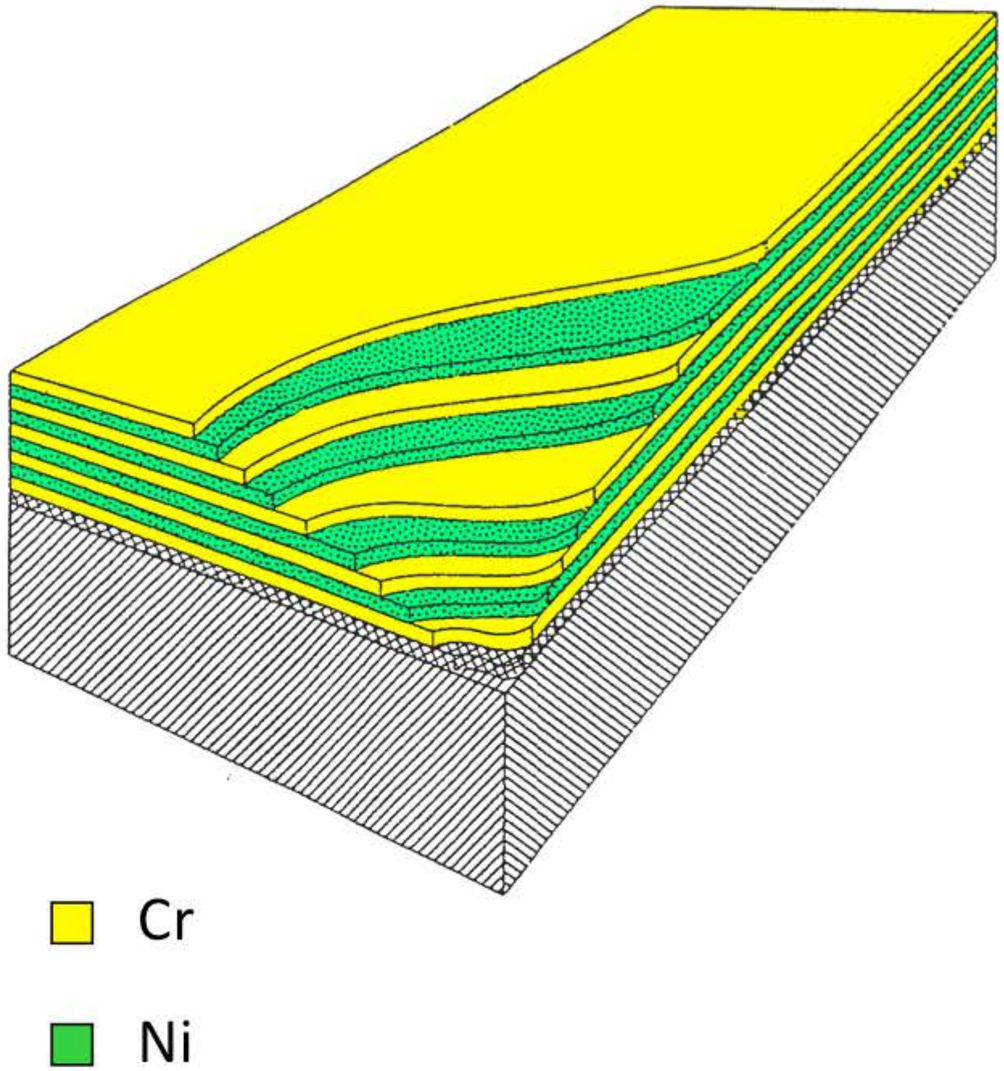




In depth profiling with fs pulses

CRM: NIST 2135c

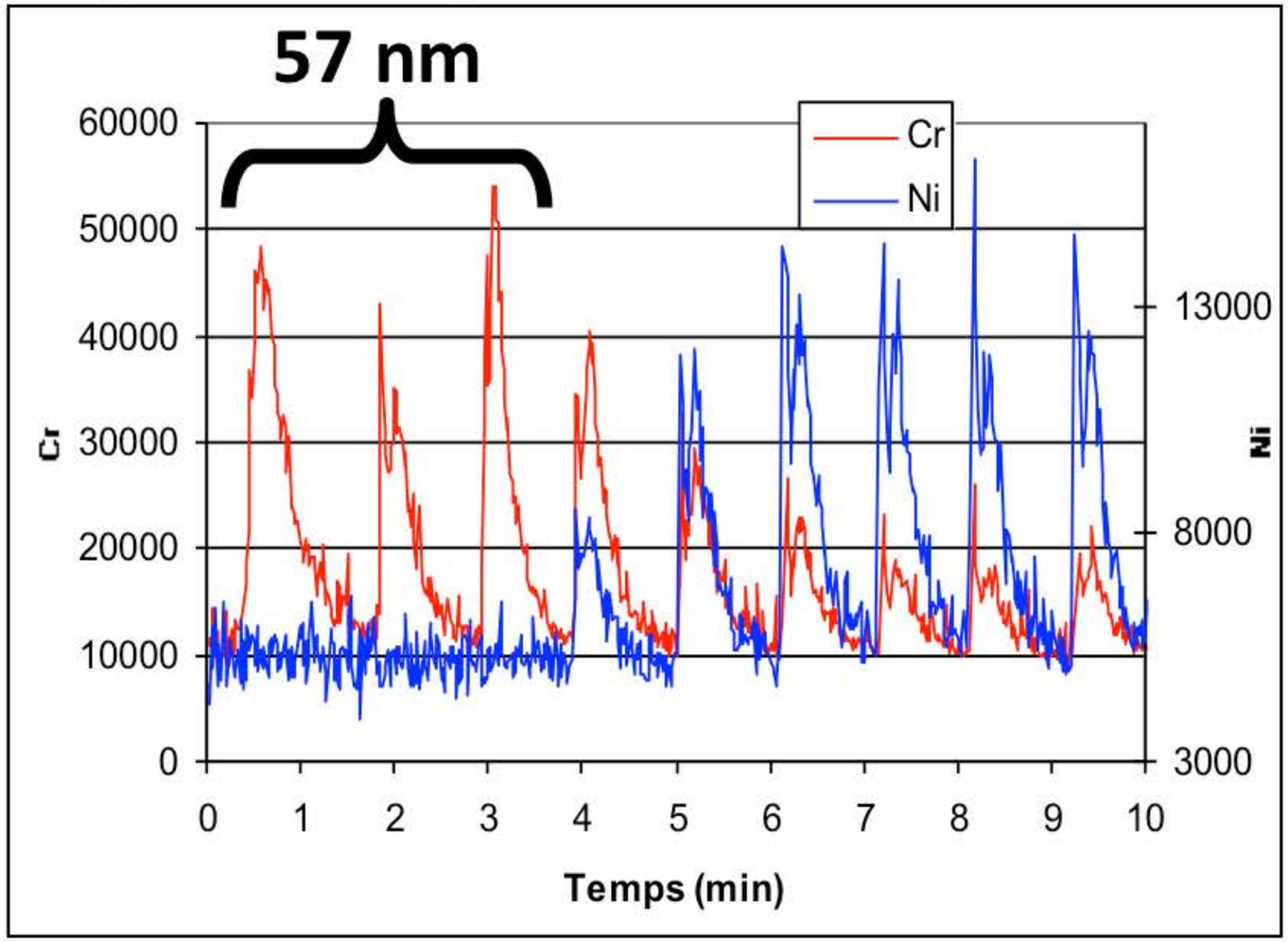
Multi layer material
Cr (57 nm) and Ni (56 nm)



⇒ **In depth resolution of about 20 nm per pulse…**

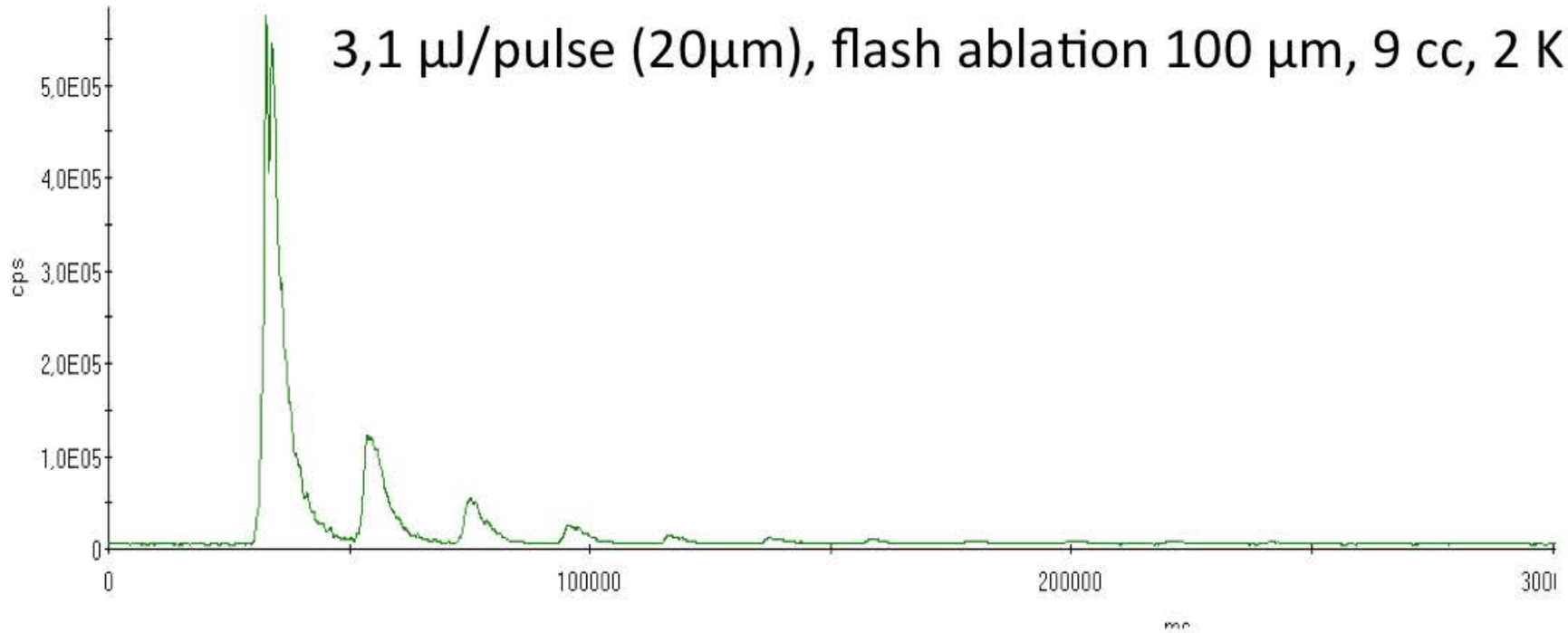
⇒ **The energy level should be adjusted close to the ablation threshold.**

⇒ **resolution though by the laser beam gaussian shape**

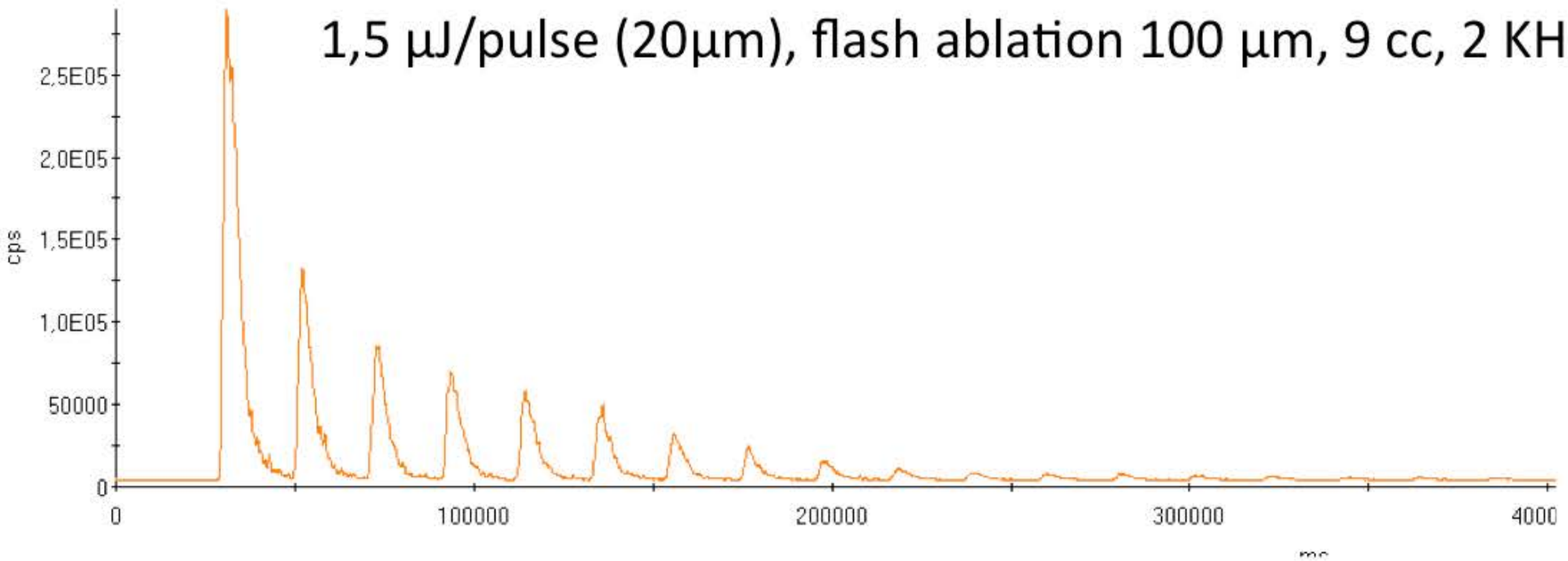


In-depth profiling with fs pulses

In depth profile of Phosphorus in a P-doped concrete



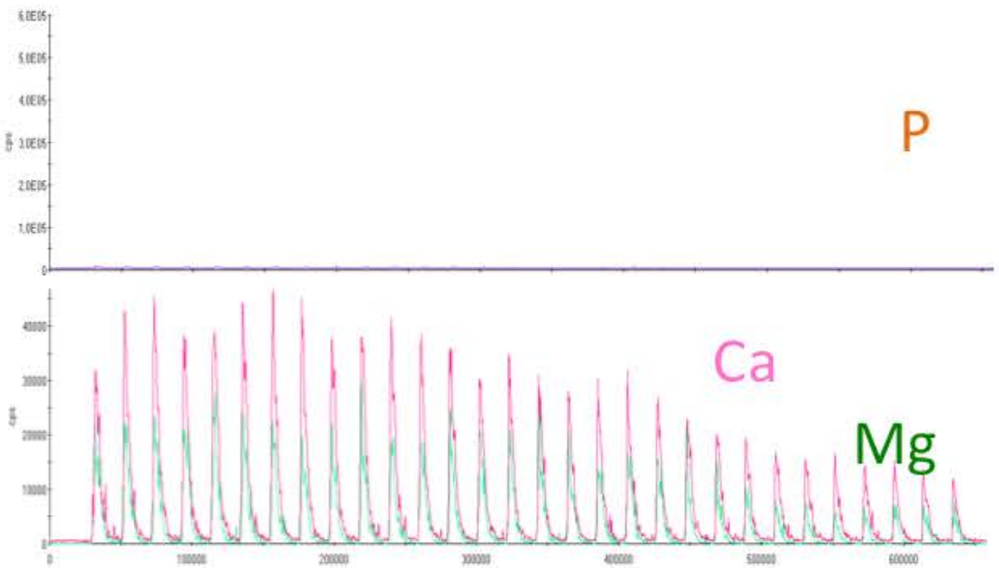
⇒ Low energy for better in depth resolution



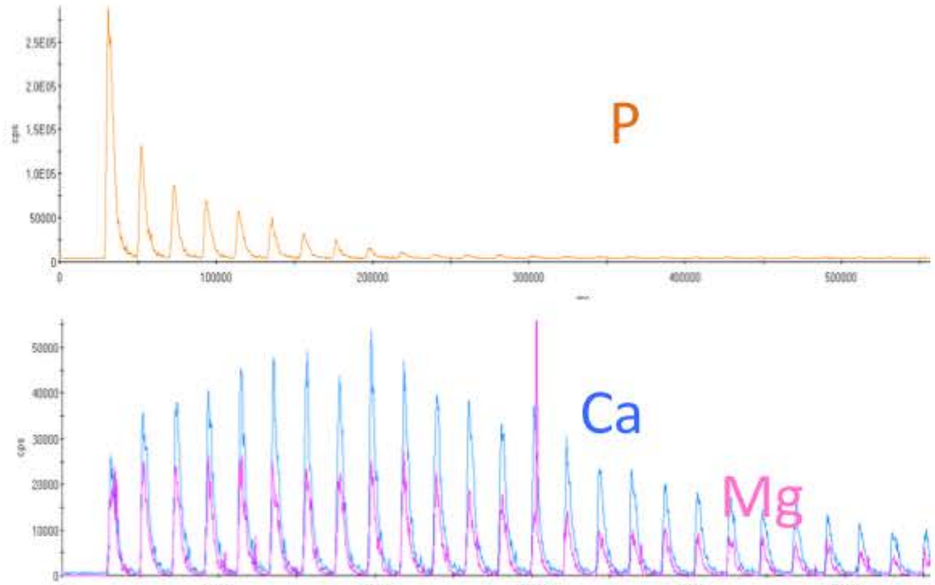
In-depth profiling with fs pulses

In depth profile of Phosphorus in a P-doped concrete

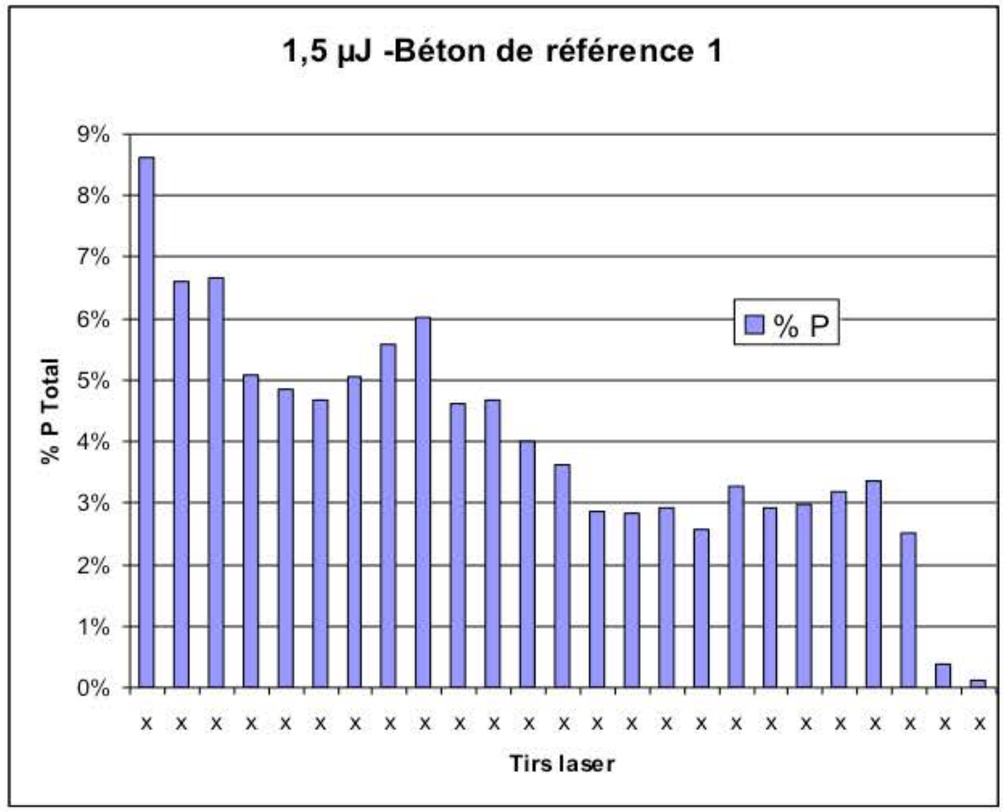
Reference concrete

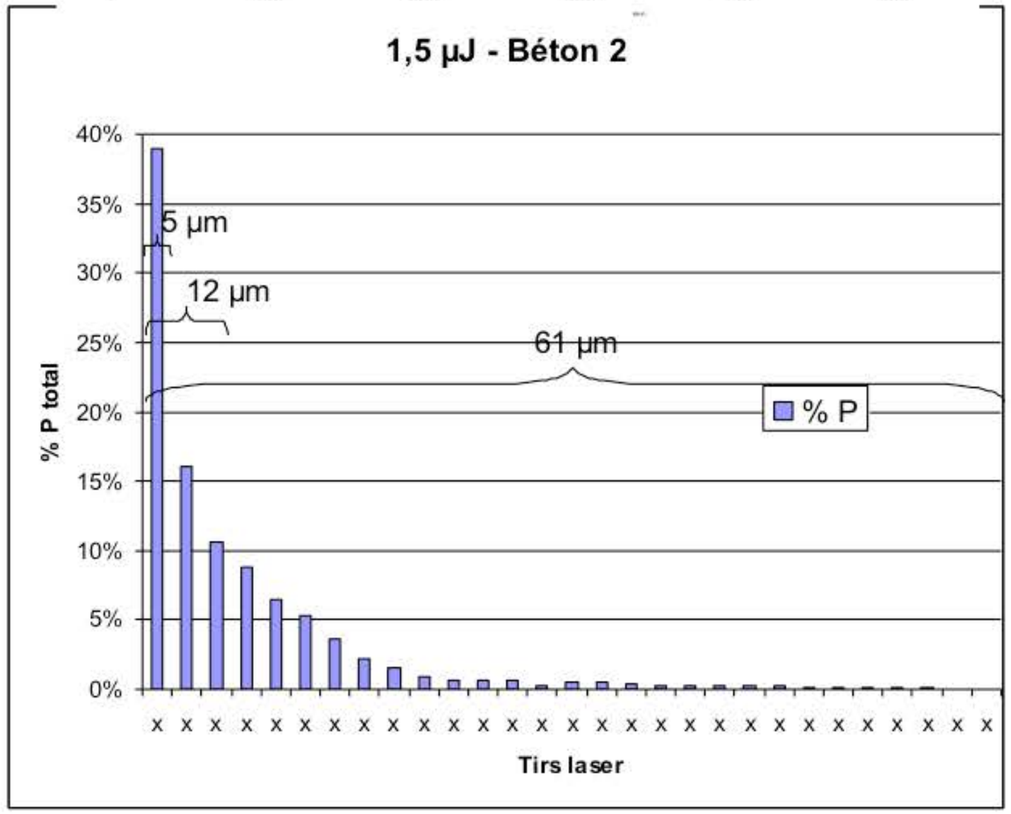


P-Doped concrete

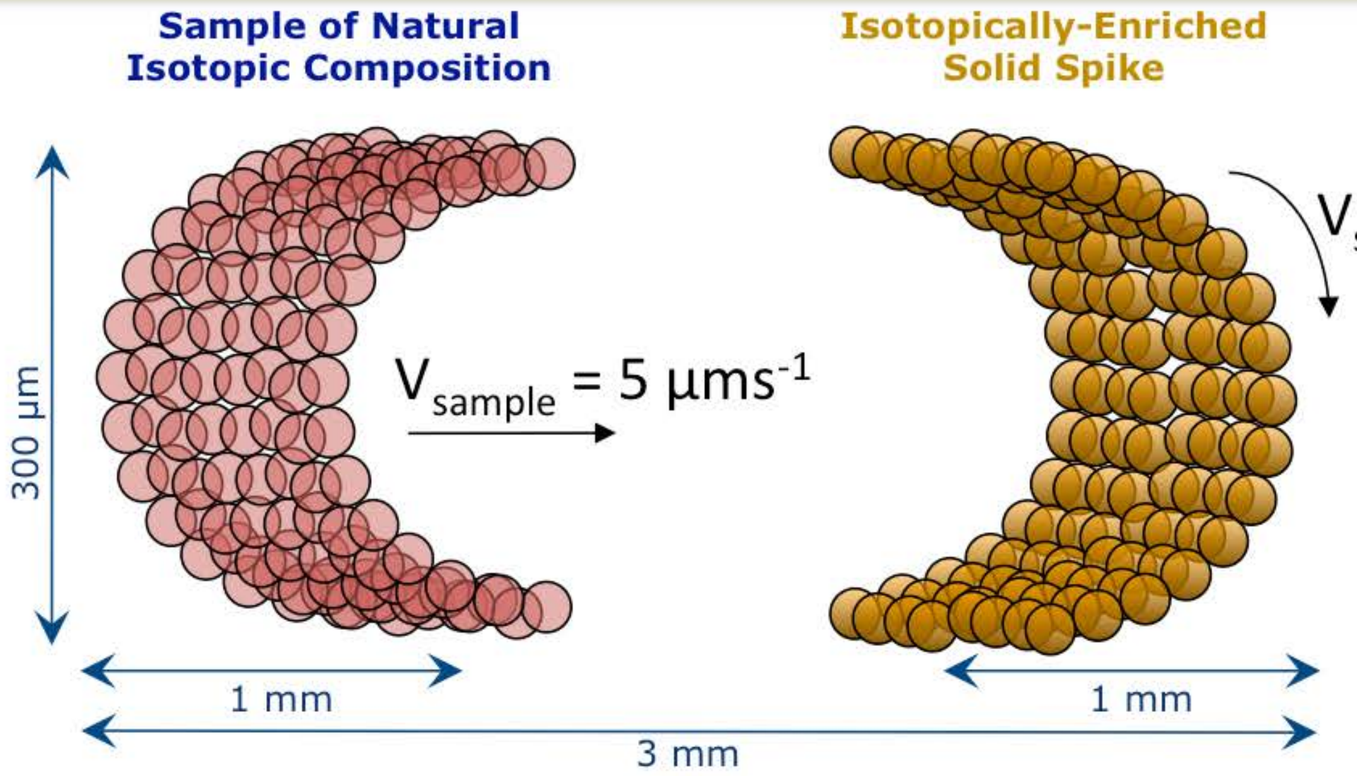


⇒ **Internal normalisation (Ca or Mg)**

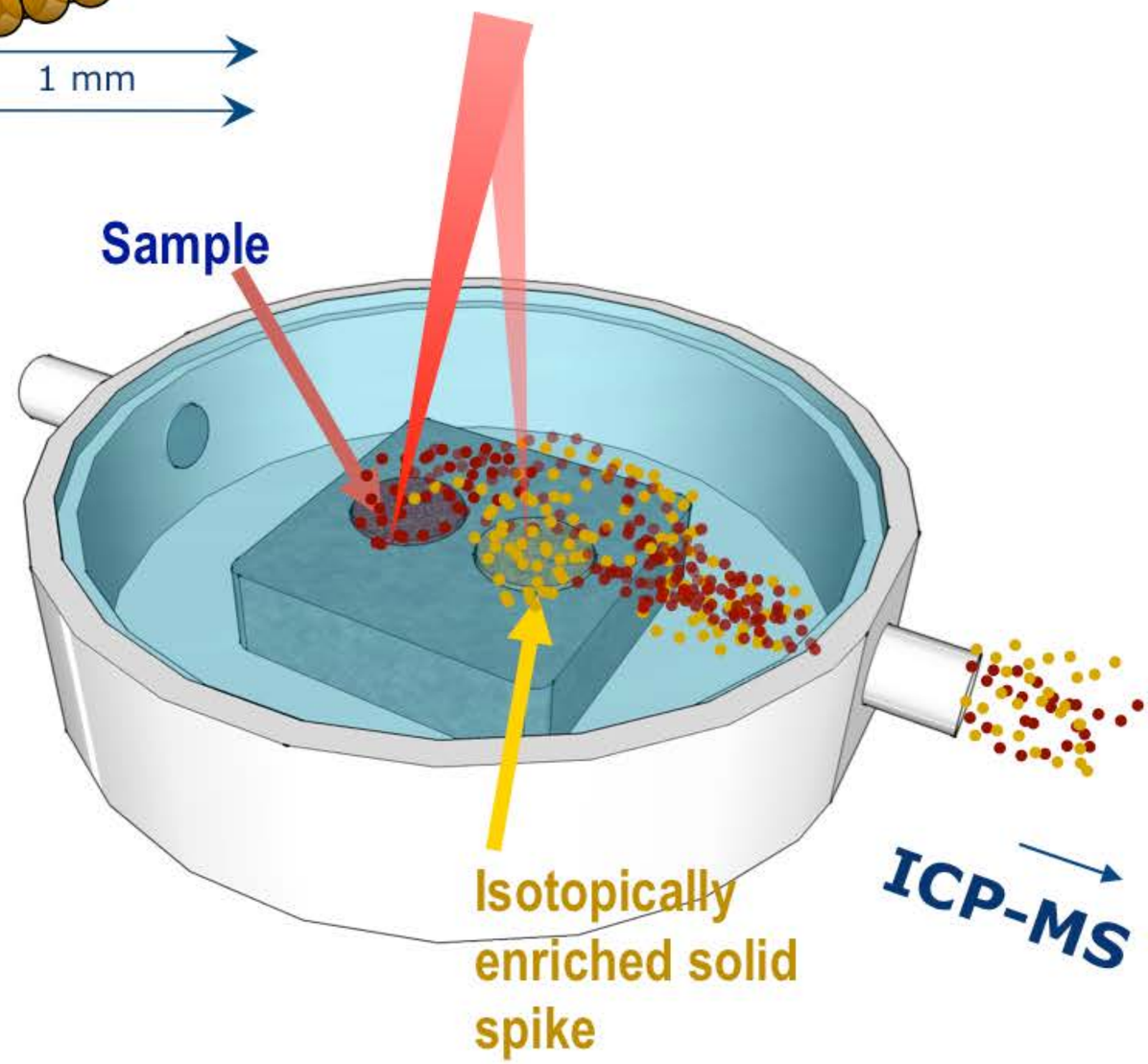




Direct in-cell Isotope Dilution analysis



Cycle : 60 ms



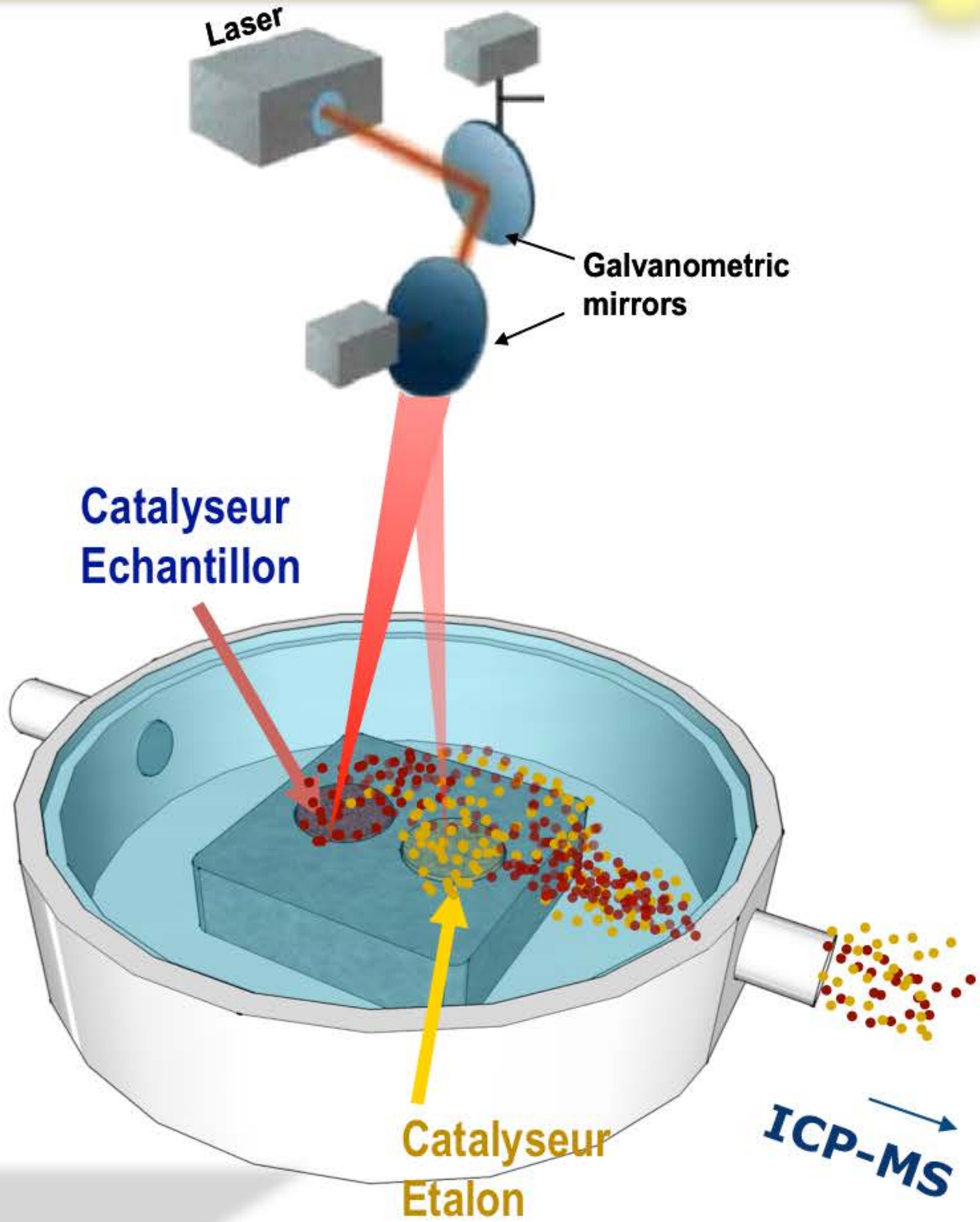
Simulating a split beam...

=> The laser beam is virtually at two places simultaneously

- ⇒ **the laser ablates simultaneously the sample and an isotopically enriched sample**
- ⇒ **the 2 aerosols are mixed into the cell**
- ⇒ **then the isotope dilution takes place into the cell**

Direct in-cell Isotope Dilution analysis

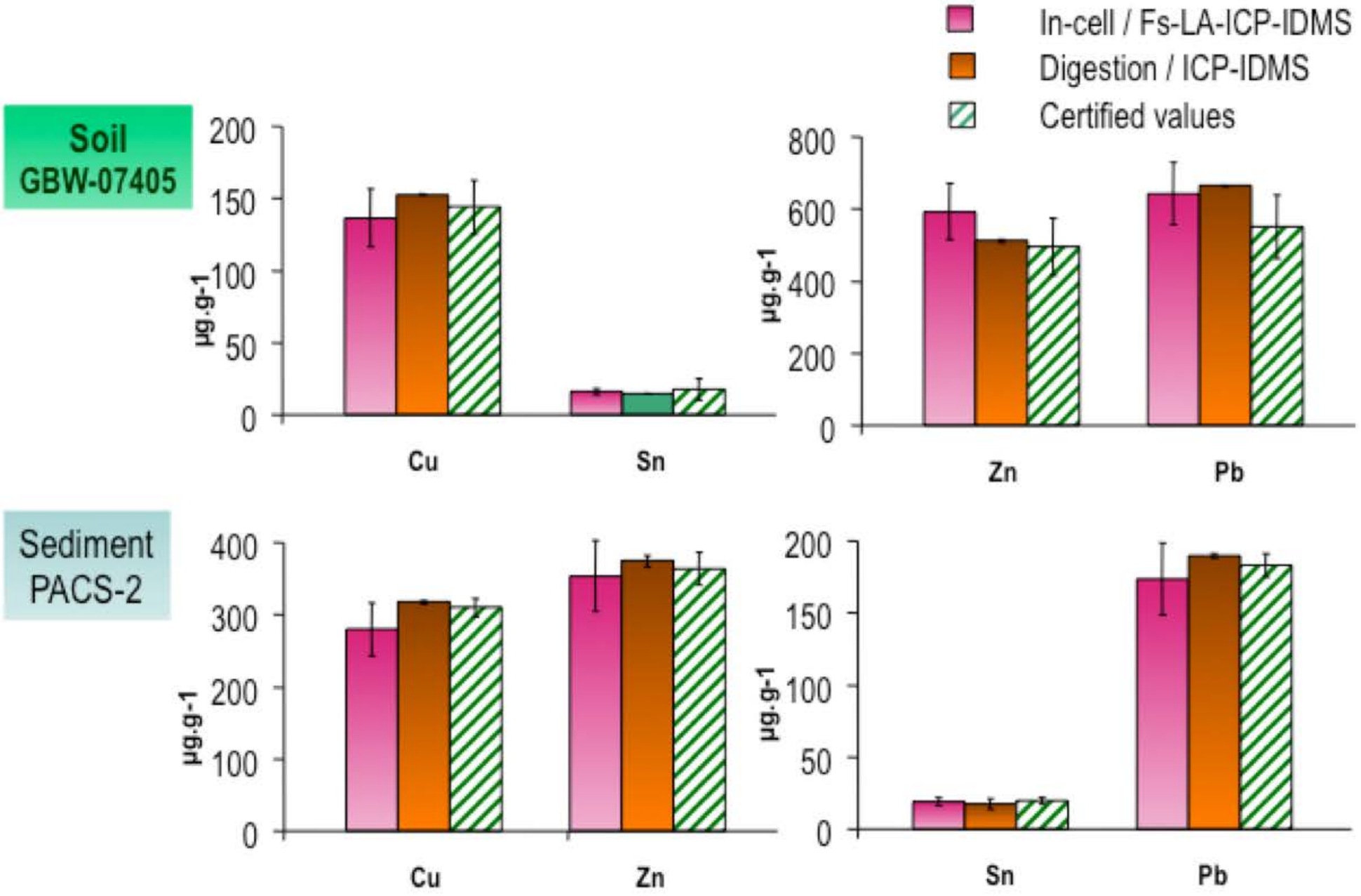
Paramètres laser	ALFAMET
pulse	360 fs
Wavelenght	1030 nm
Repetition rate	1000 Hz
Energiy	45 µJ
Scanner speed (ablation)	1 $mm.s^{-1}$
Scanner jump	100 $mm.s^{-1}$
virtual beam shape	150 µm
Distance between 2 pellets	1 mm



Direct In-cell isotope dilution

In-cell ID/ICPMS
< 6 min

Conventional ID/ICPMS
6 Hours



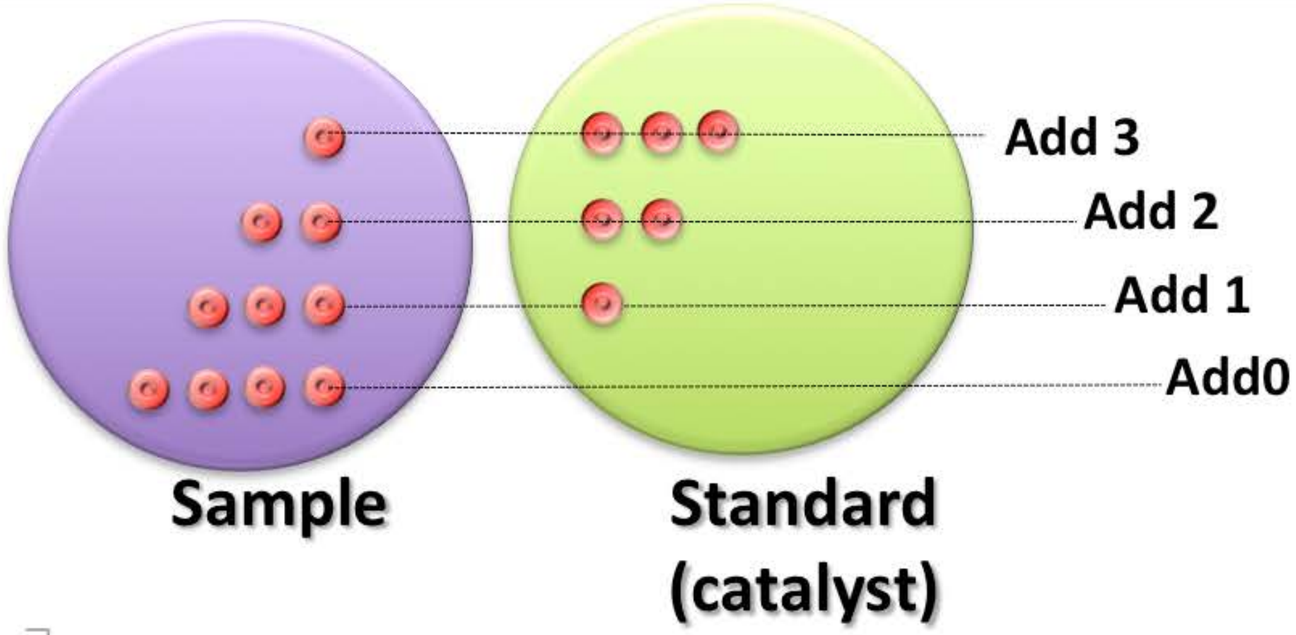
APPLICATION TO SOILS AND SEDIMENTS ANALYSIS

⇒ **in 6 min vs 6 hours**

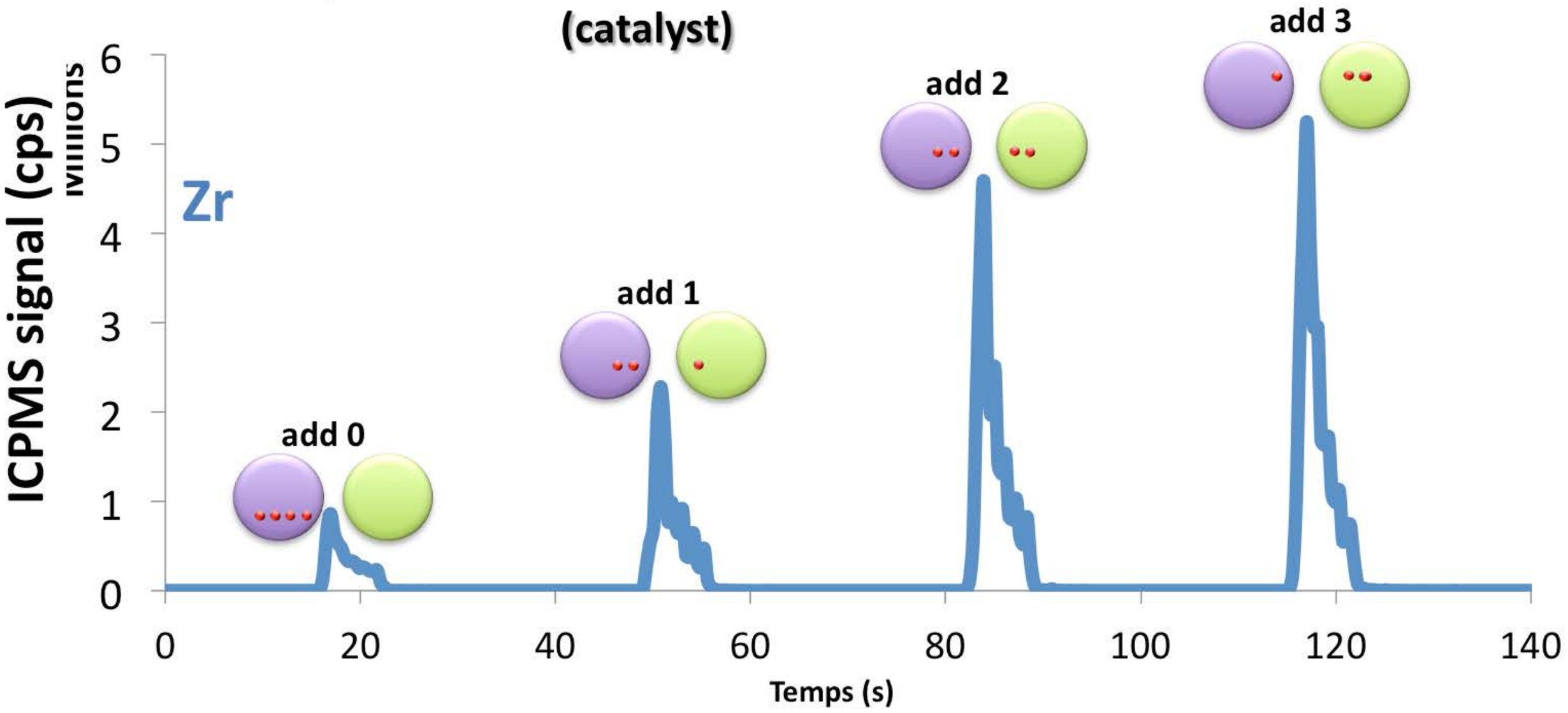
⇒ **limitations due to sample inhomogeneity**

Fernandez et al, Anal. Chem. 2008, 80, 6981-6994

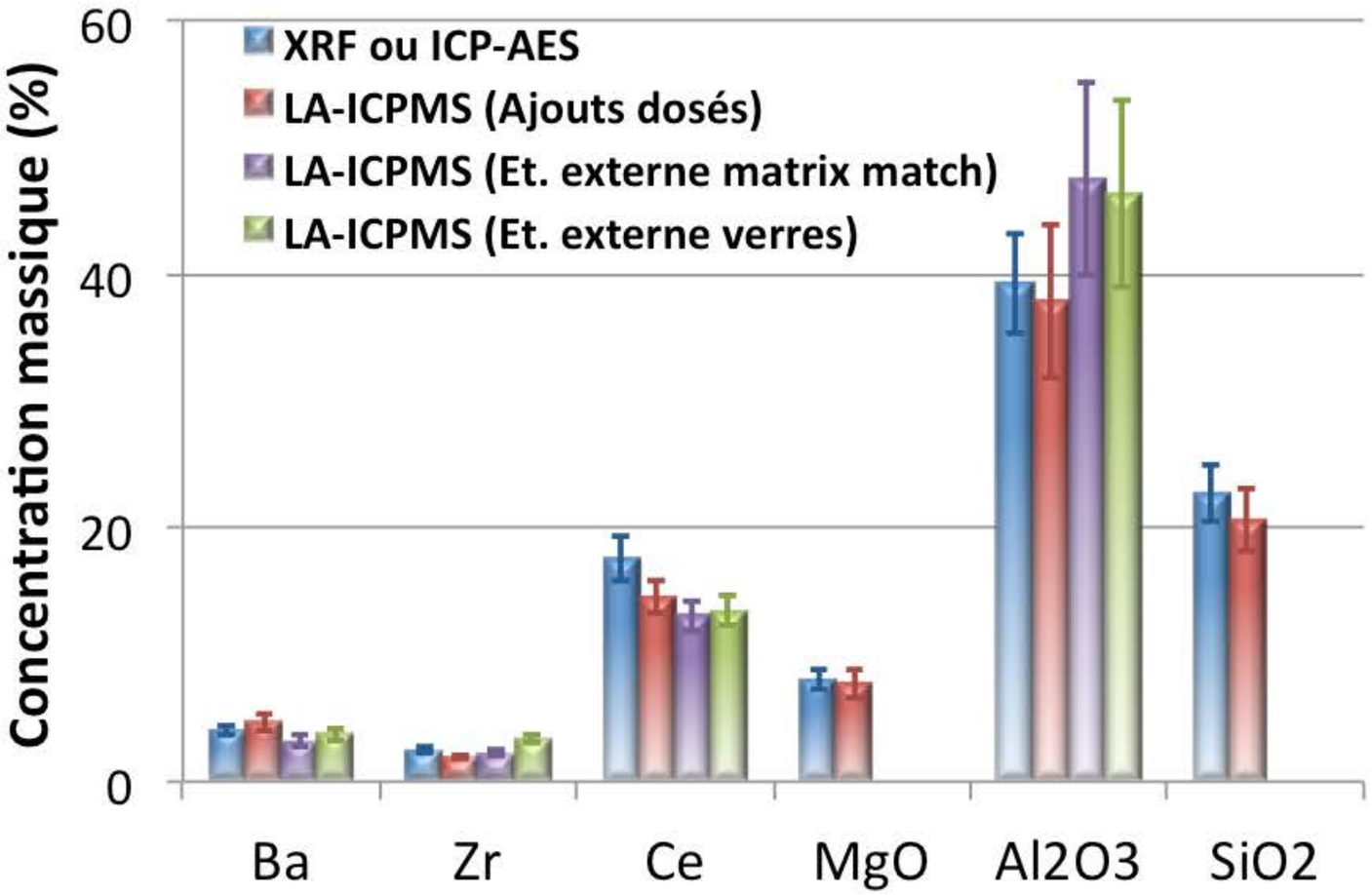
Direct In-cell standard addition

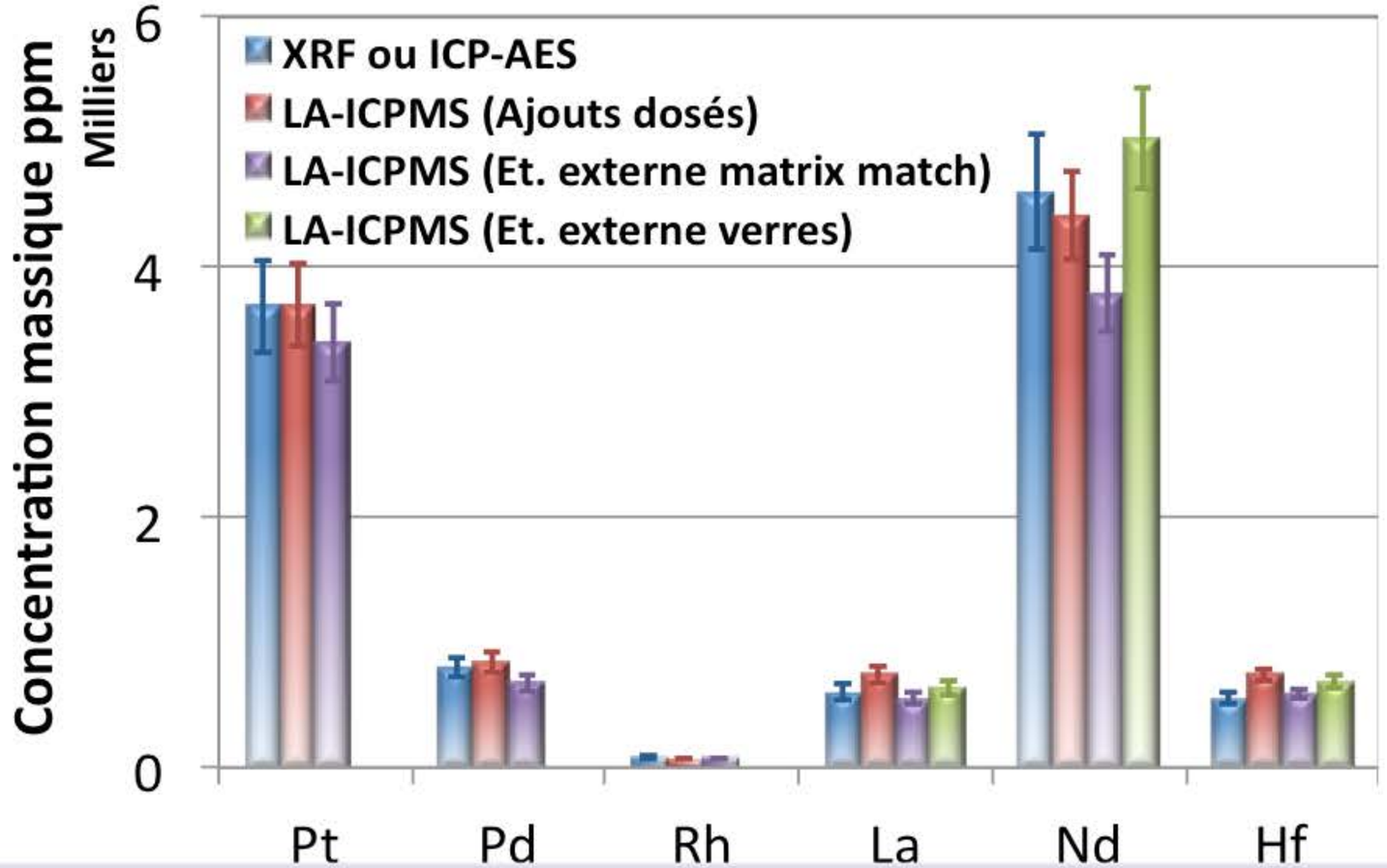


- Constant nb of shots
- **Identical ablation yield from one pellet to the other**



Validation

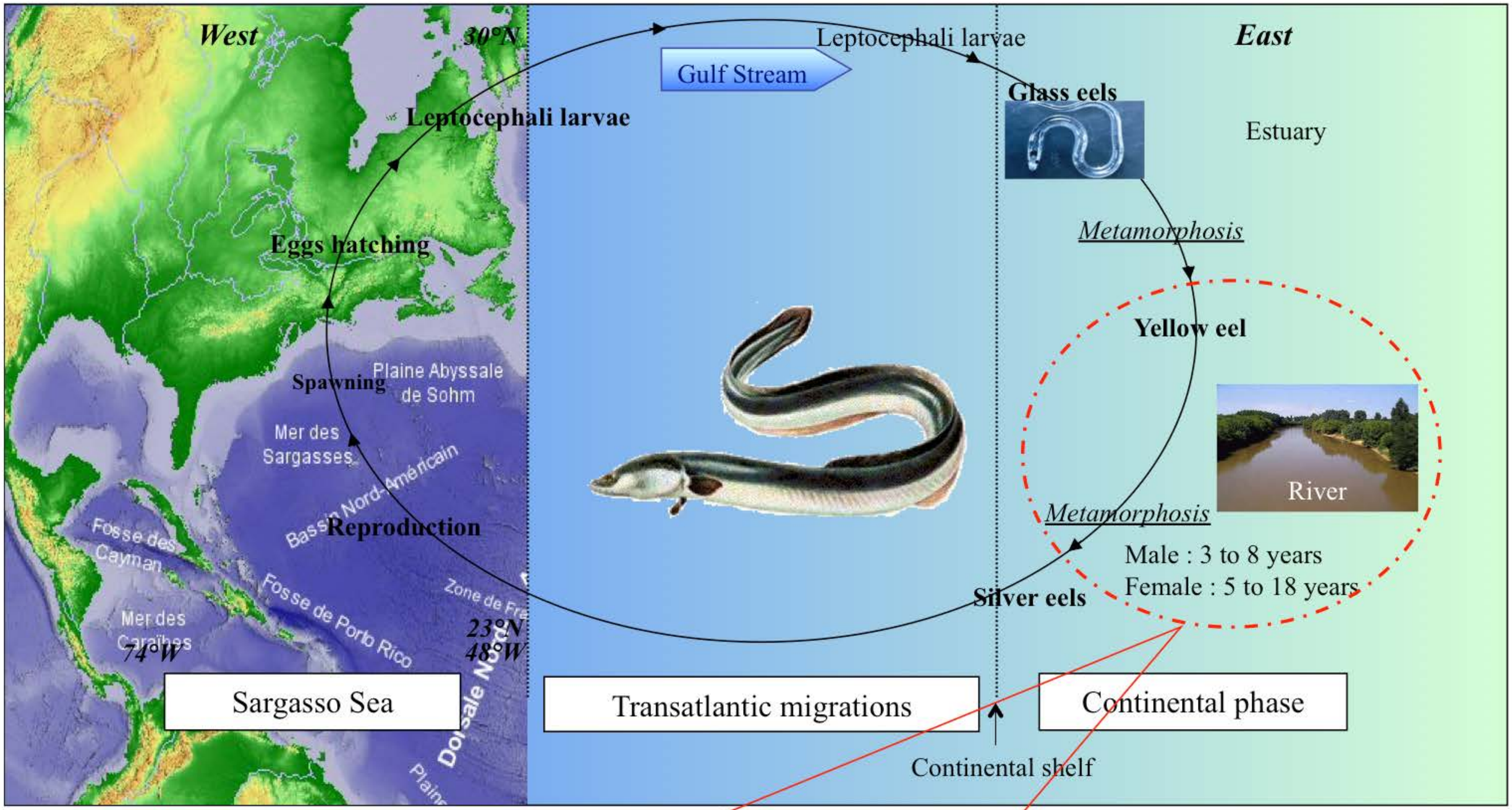

Concentration massique (%)
60
40
20
0
XRF ou ICP-AES
LA-ICPMS (Ajouts dosés)
LA-ICPMS (Et. externe matrix match)
LA-ICPMS (Et. externe verres)
Ba
Zr
Ce
MgO
Al2O3
SiO2


Concentration massique ppm
Milliers
6
4
2
0
XRF ou ICP-AES
LA-ICPMS (Ajouts dosés)
LA-ICPMS (Et. externe matrix match)
LA-ICPMS (Et. externe verres)
Pt
Pd
Rh
La
Nd
Hf

Application of the virtual beam shaping to biocarbonate analysis

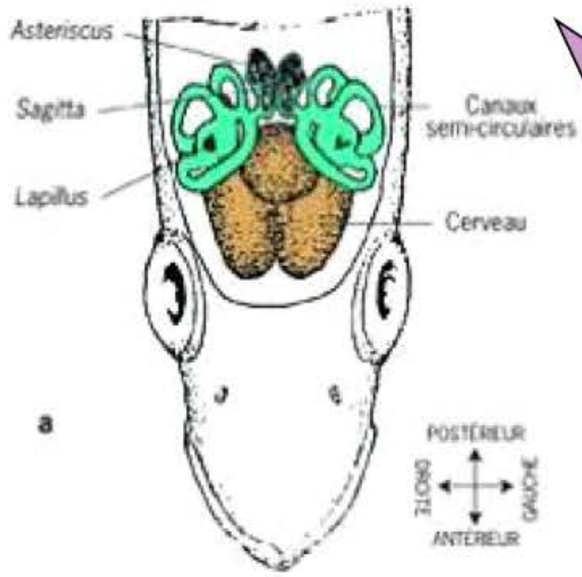
European eel *Anguilla anguilla* : biological cycle

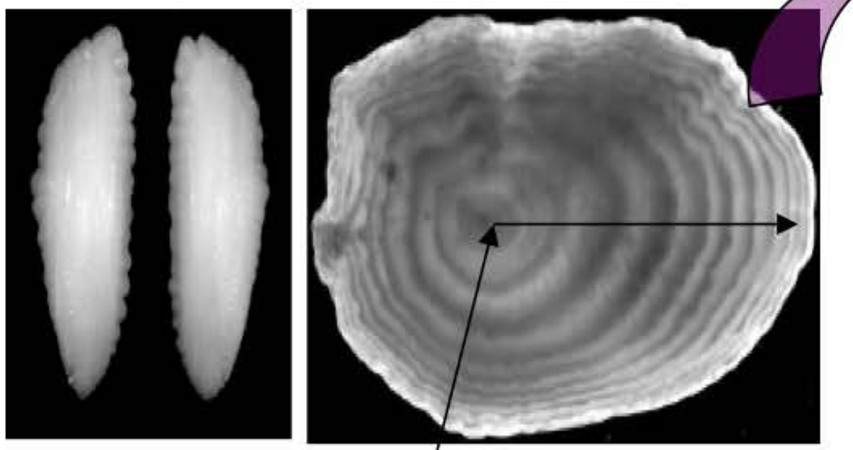
- **Ubiquitous declining species with great local and european economical stakes**
- **Long live predator, high fat content, high resistance to physico-chemical conditions.**



Anthropogenic activity influence on the Adour ecosystem : eel as a model

Markers of physico-chemical condition : from the molecular response level to the reconstruction of the individual history through the otolith





Growing striae (aragonite)

=> time scale

Analysis of trace element in eels otoliths as a tracer of migration

High spatial resolution and sensitive analytical technique LA-ICPMS

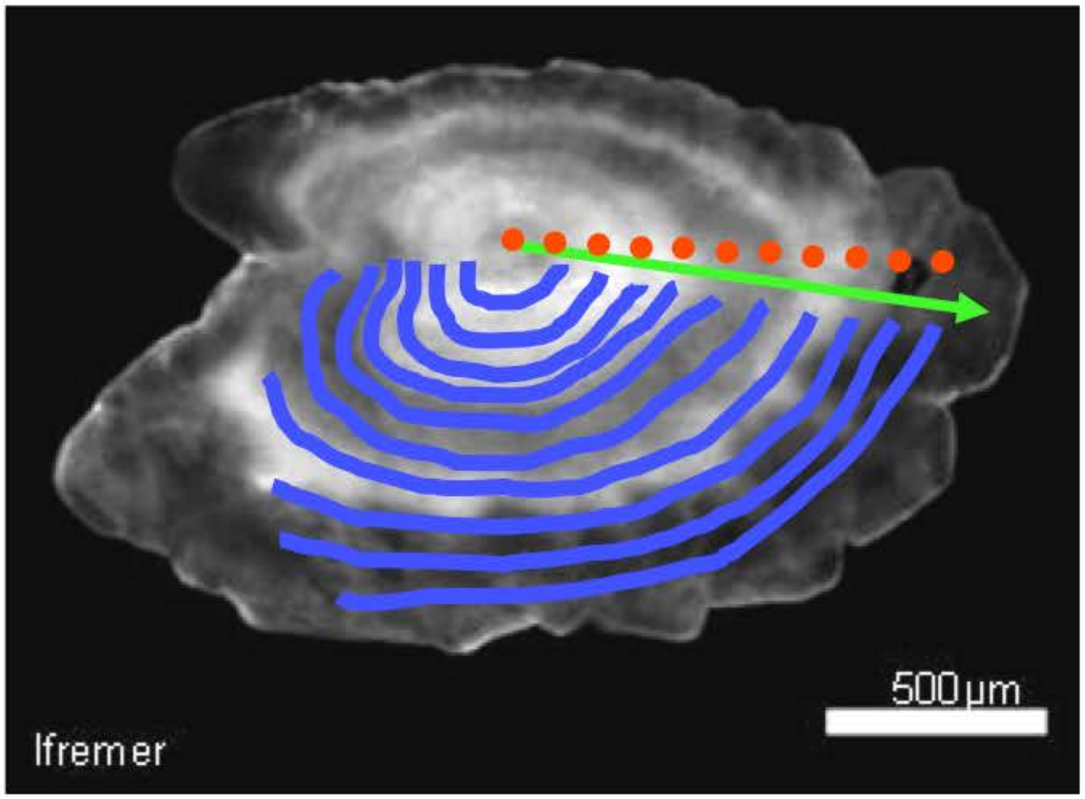
Trace element and isotope microchemistry

Ba, Sr, Mg, Mn, Zn, Cd, Pb, Li, Ca...

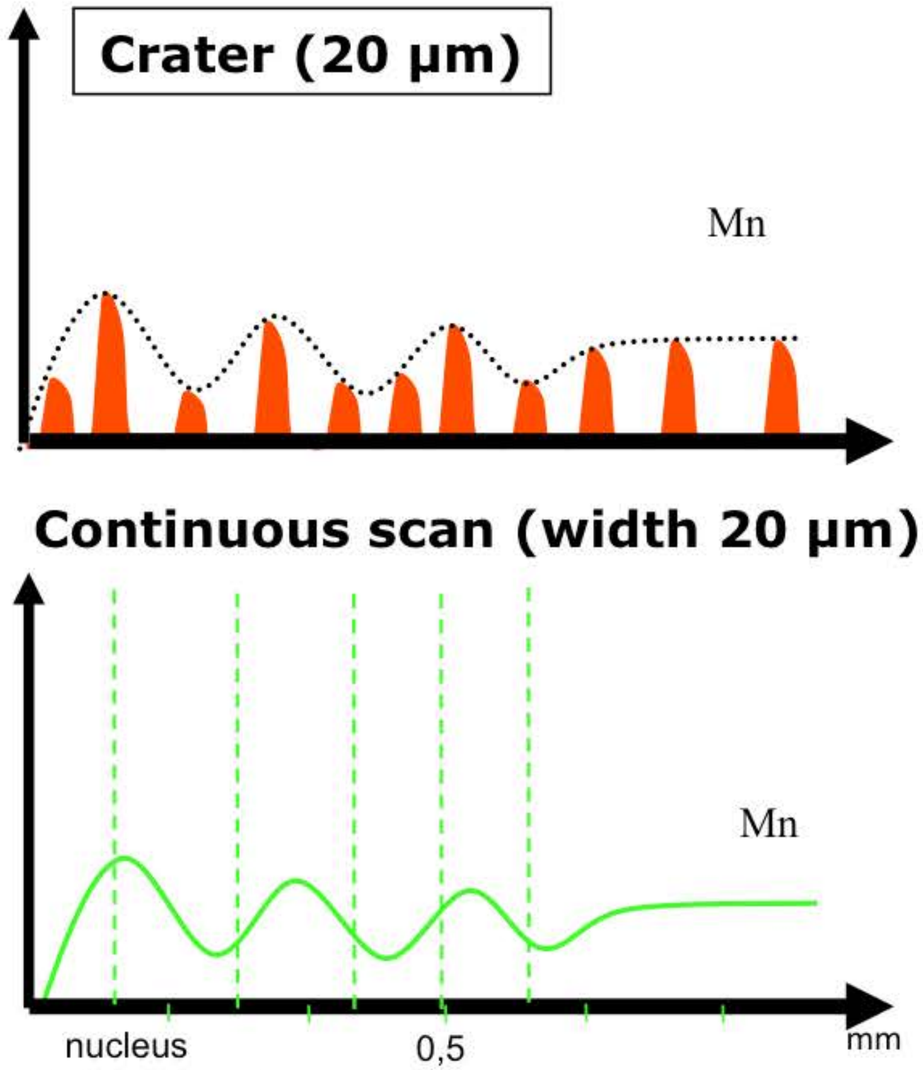
$^{87}Sr/^{86}Sr$

Virtual beam shaping

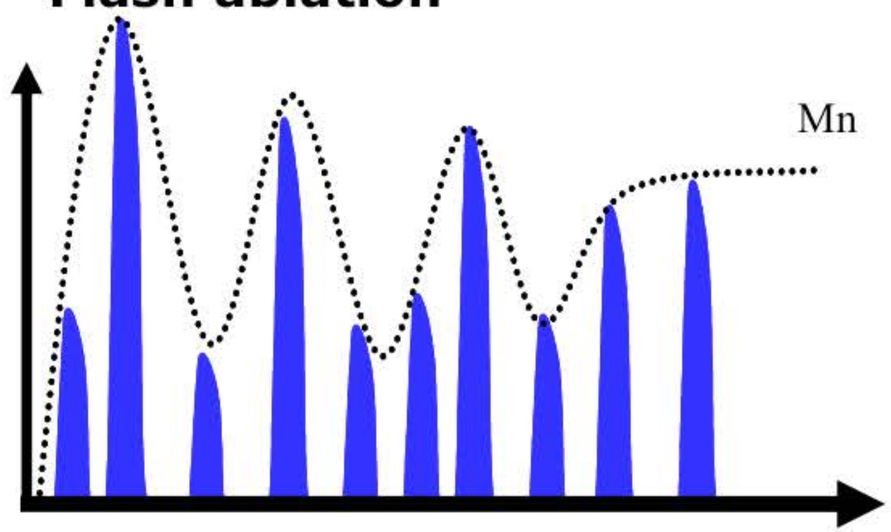
Increasing the ablation rate to improve the signal to noise ratio…



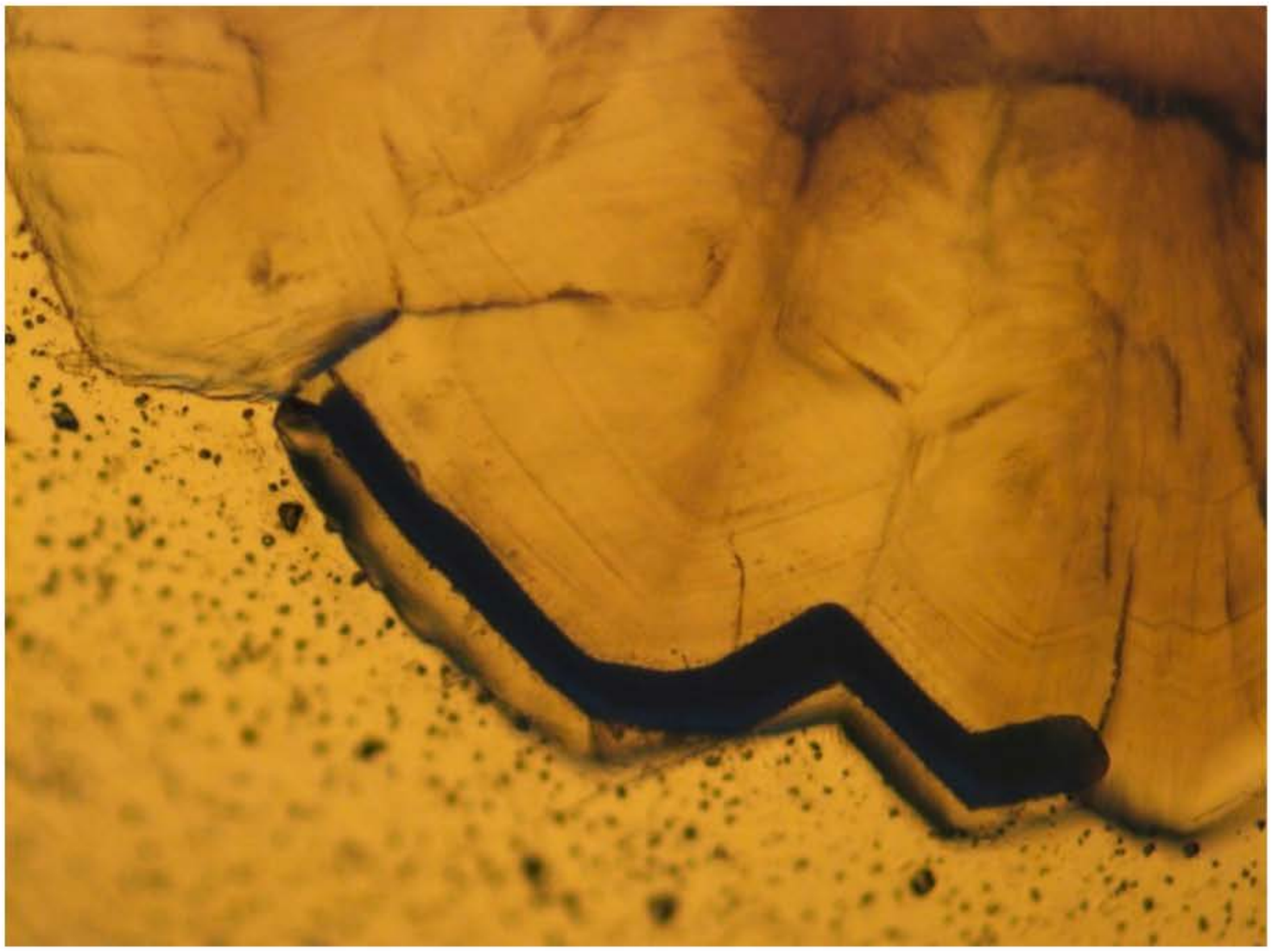
Trace element detection



Flash ablation



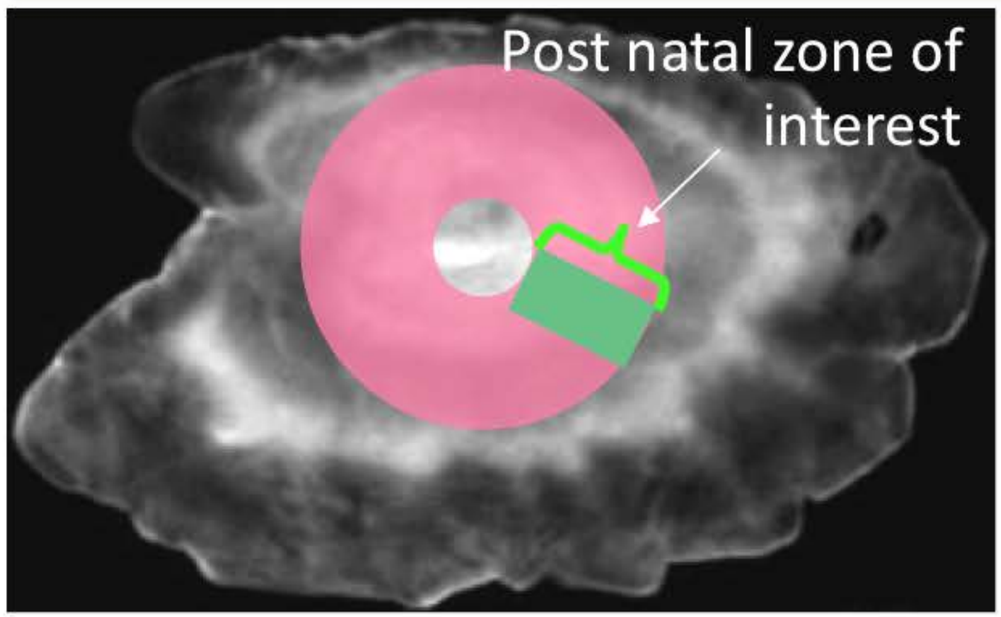
Flash ablation to understand a given life-time history



Otolith border

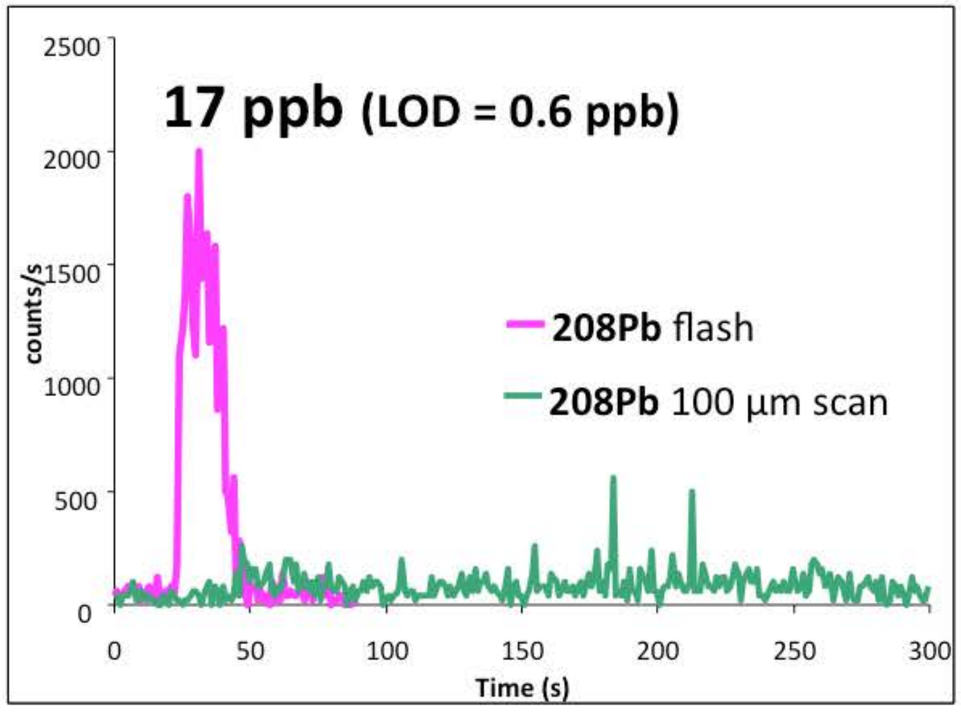
= sampling place

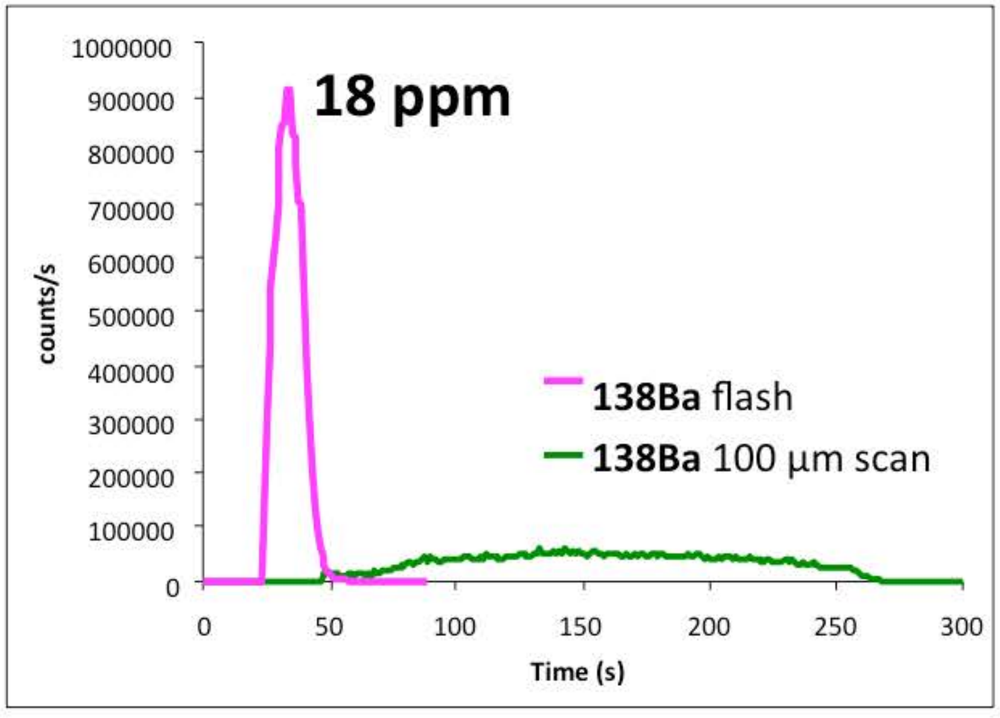
Flash ablation to understand a given life-time history



Flash ablation of the post natal growing zone for high sensitivity…

Ablation rate $_{\text{flash}}$ = 20 x Ablation rate $_{\text{scan}}$



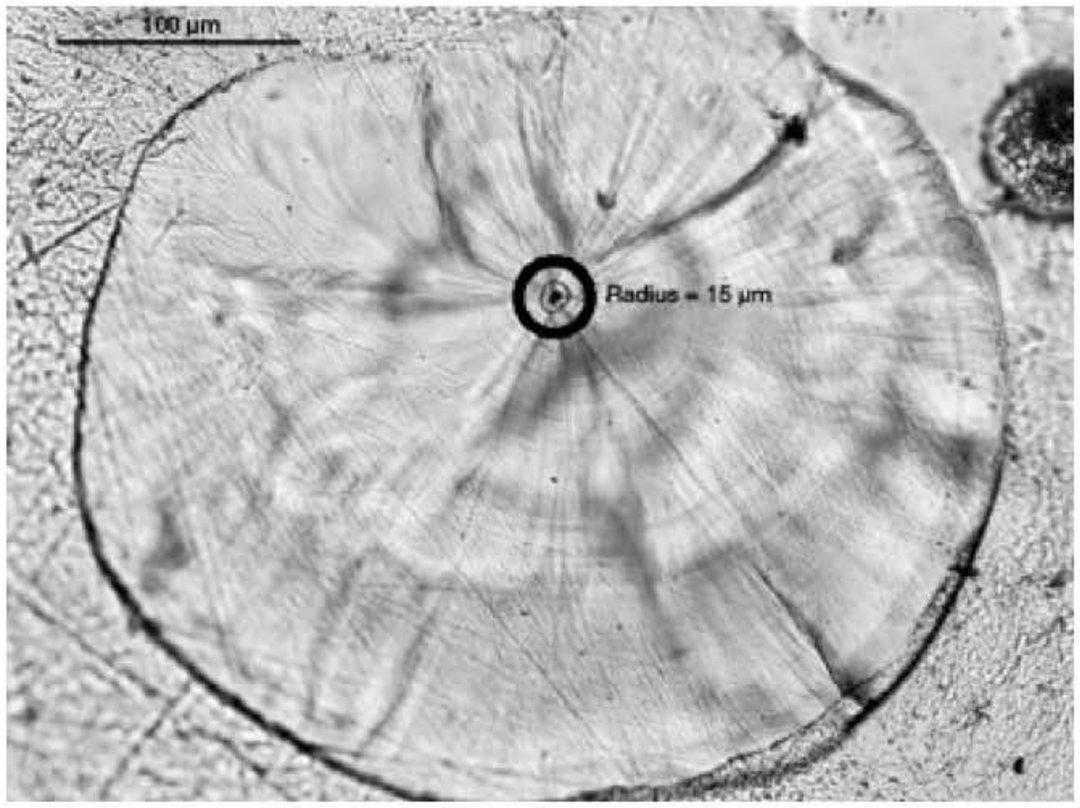


Simulating a corona-shape laser beam

Perrier et al, Can. J. Fish. Aquat. Sci. 68: 977–987 (2011)

*Fig. 2. Pictures of (**a**) juvenile and (**b**) adult Atlantic salmon otoliths showing the area ablated by the laser prior to inductively coupled plasma mass spectrometry analysis. The annulus ablated is 200–600 µm, is centered on the primordium, and corresponds to the juvenile period of growth only.*

Simulating a corona-shape laser beam



Corona ablation around the nucleus to avoid the mother's signature => place of birth

Martin et al, Ecology of Freshwater Fish, 2010

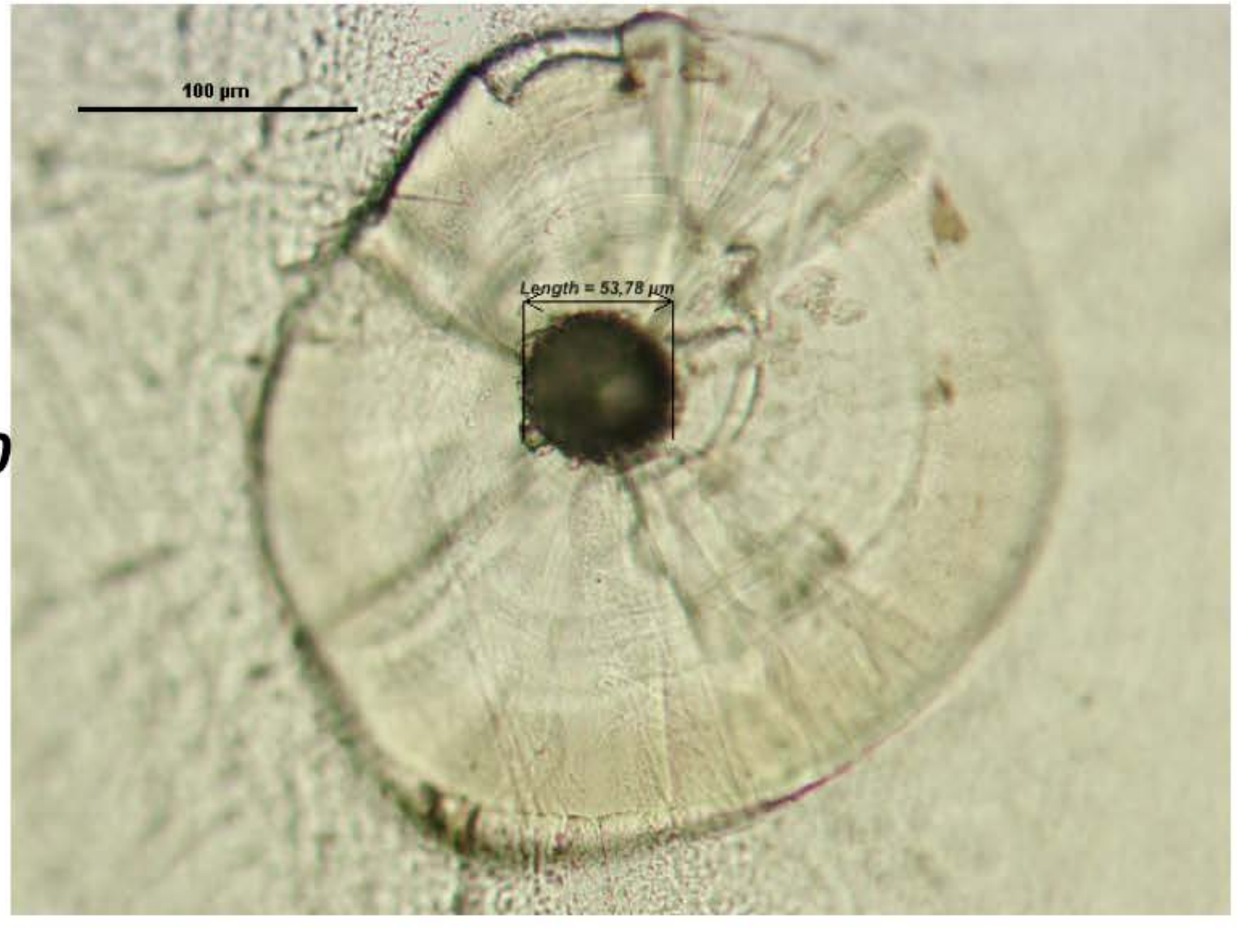
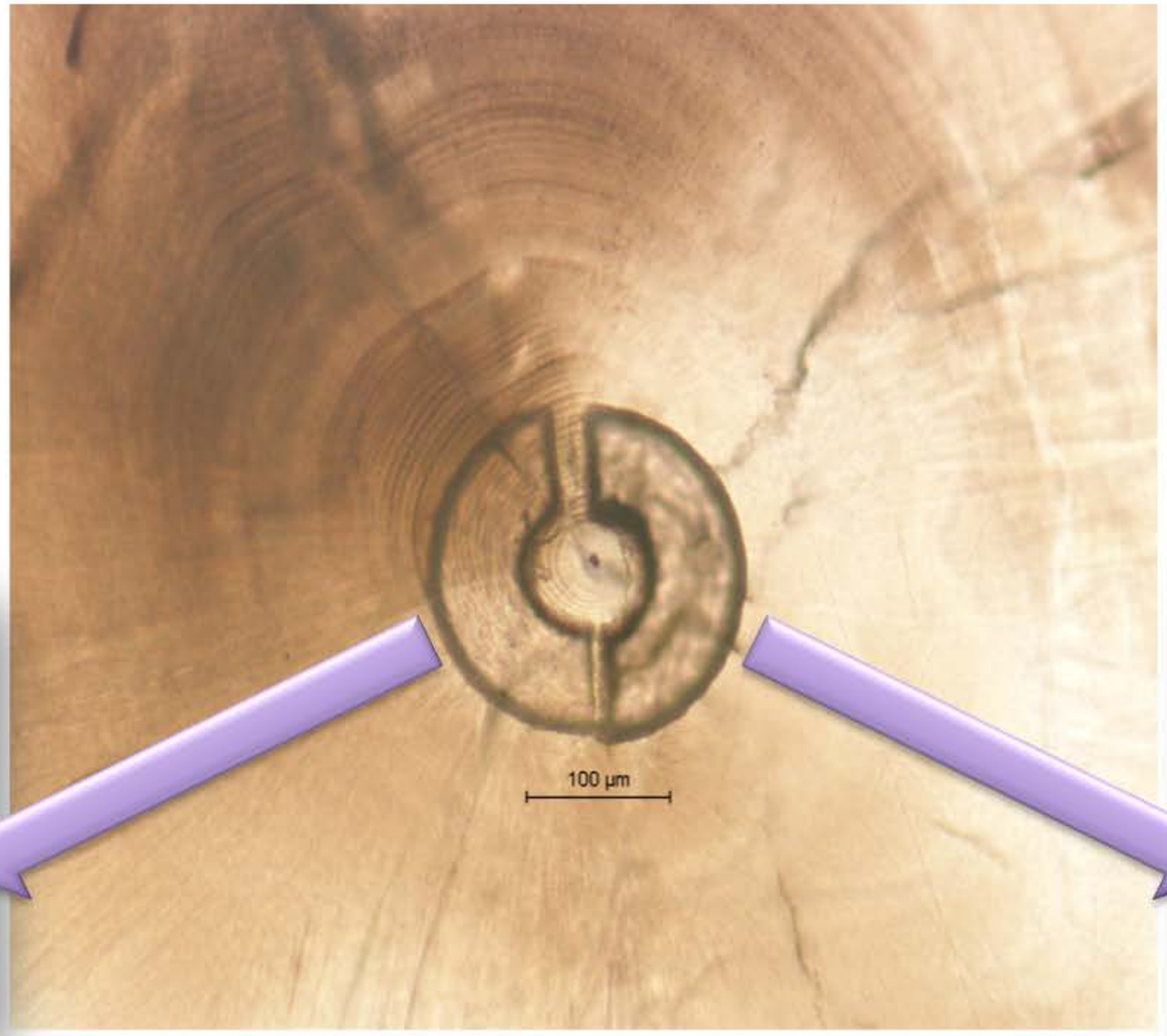


Fig. 3. Representative otolith image with an annular ablation trajectory along the first feeding mark (15 µm away from the primordium) - *Eel*.

Simulating a semi corona-shape laser beam

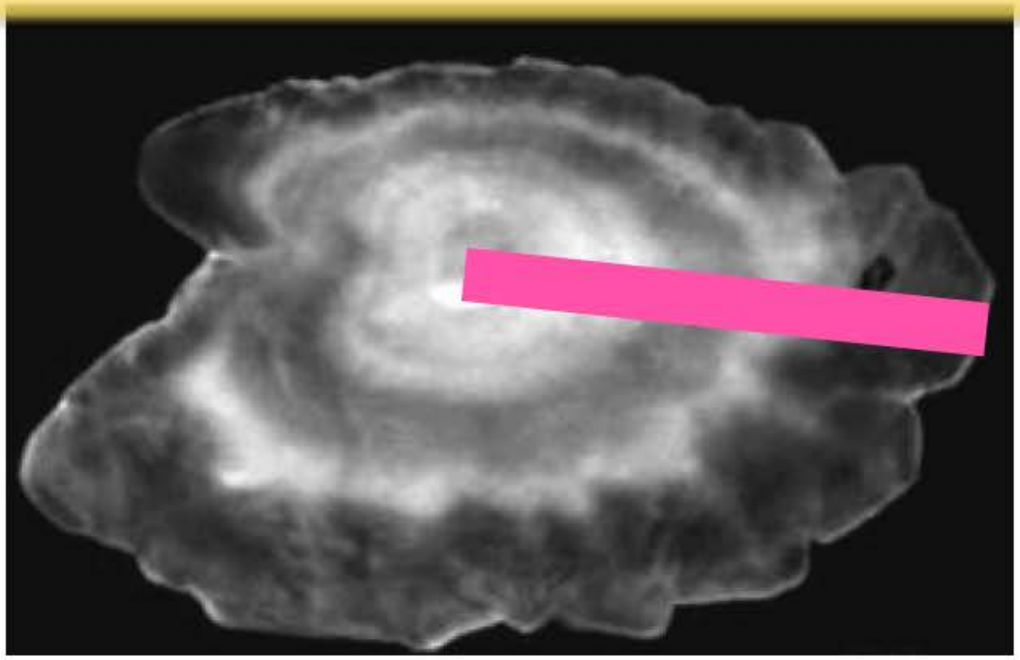


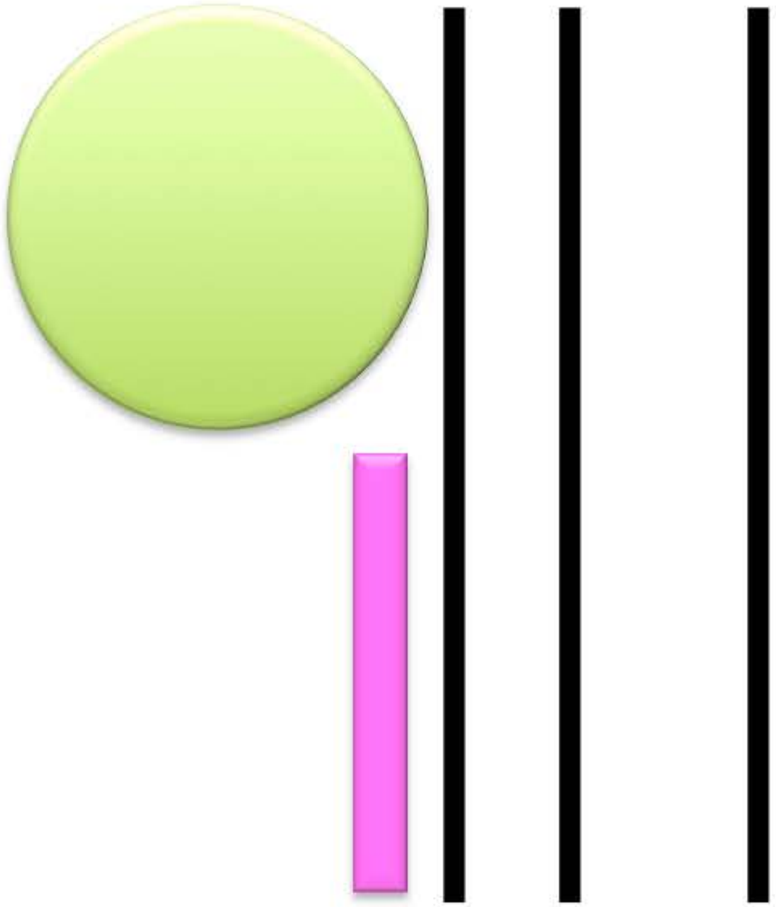
Alosa

Trace metal analysis
Ba, Sr, Mg, Mn, Zn, Cd, Pb, Li, Ca...

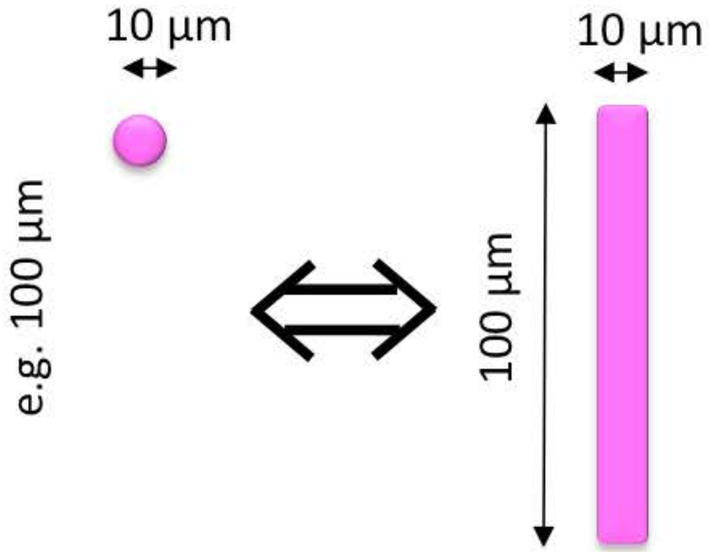
Isotope distribution
$^{87}Sr/^{86}Sr$, ...

Simulating a sharp blade laser beam

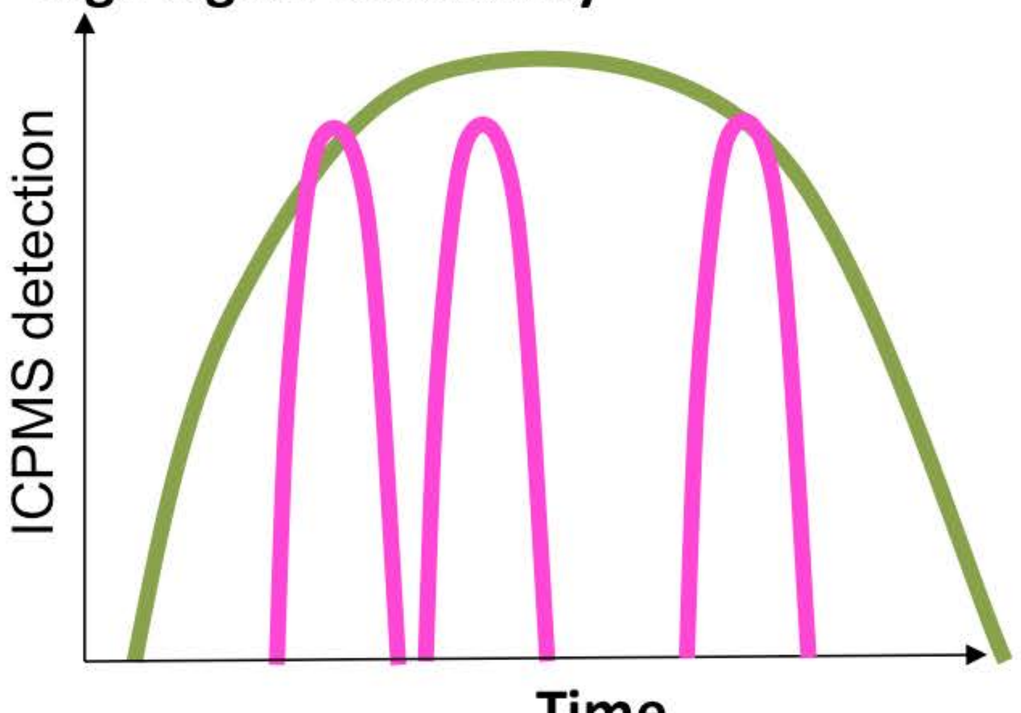




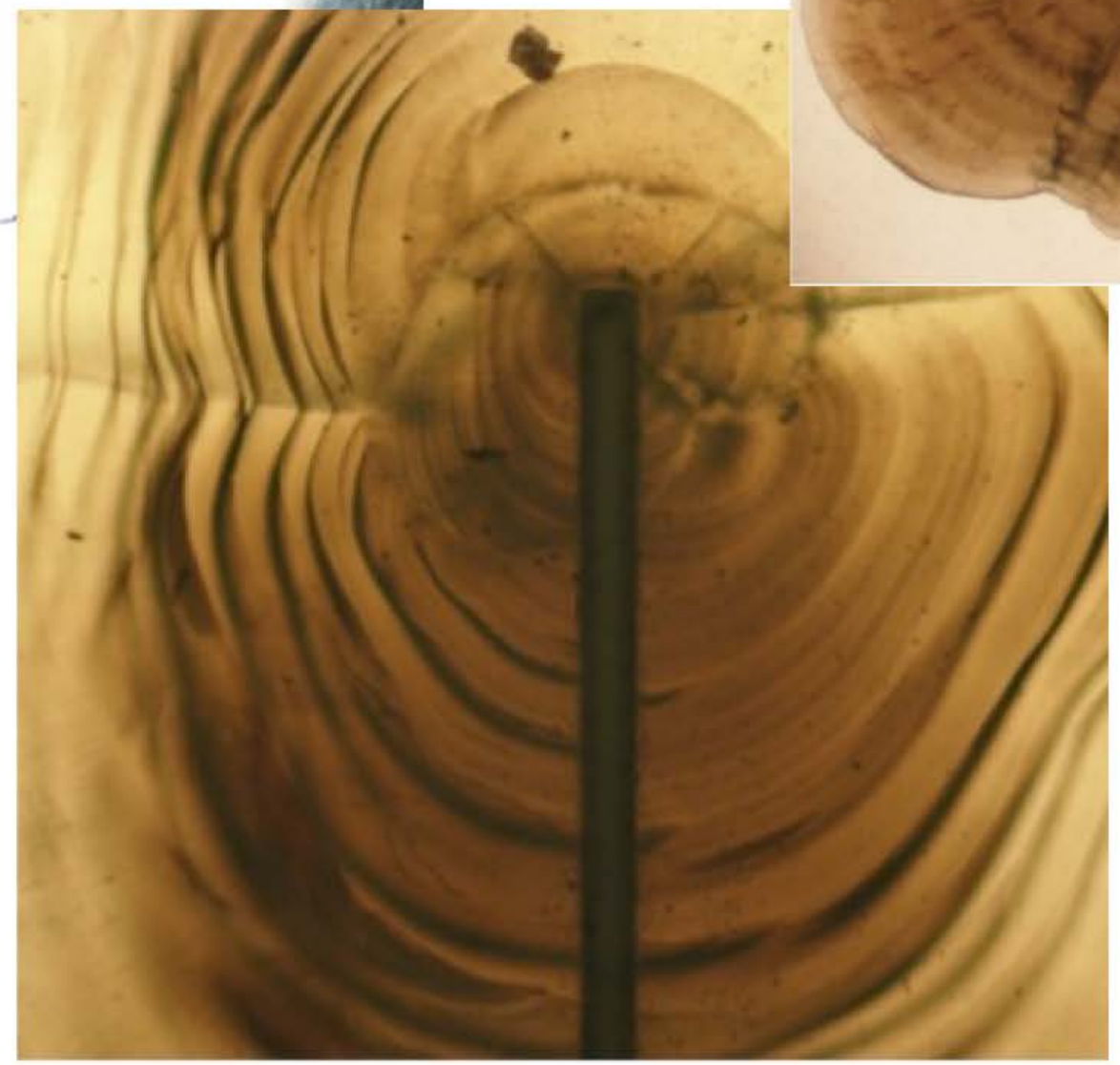
Scanning with a virtual sharp blade…



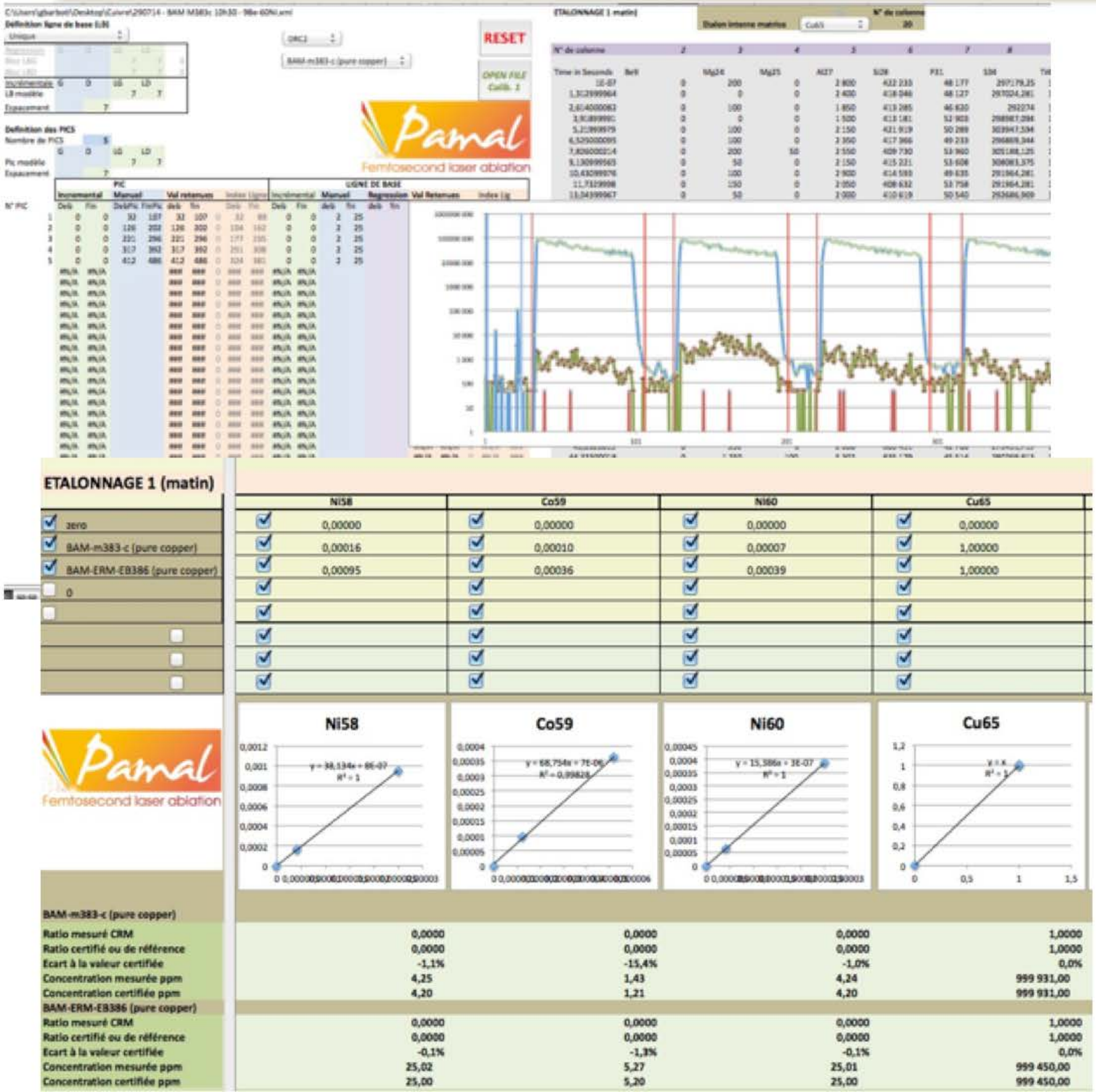
Large spot vs sharp blade ablation :
-> better spatial resolution while keeping high signal sensitivity



Sharp blade ablation scan, growing axis, life history



Quantitation and quality control

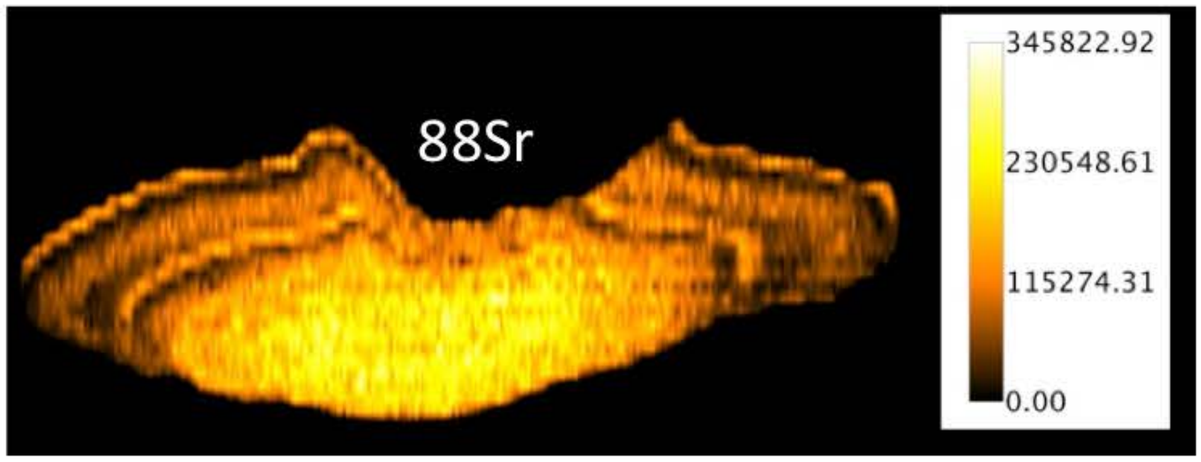


We have developed our own VBA Macro working with Excel (FOCAL series) for data processing and quantification. FOCAL series allows rapid quantification with quality control tools for the various laser ablation approaches : ablation lines (continuous scan across a sample, spot ablation, rasters for imaging).

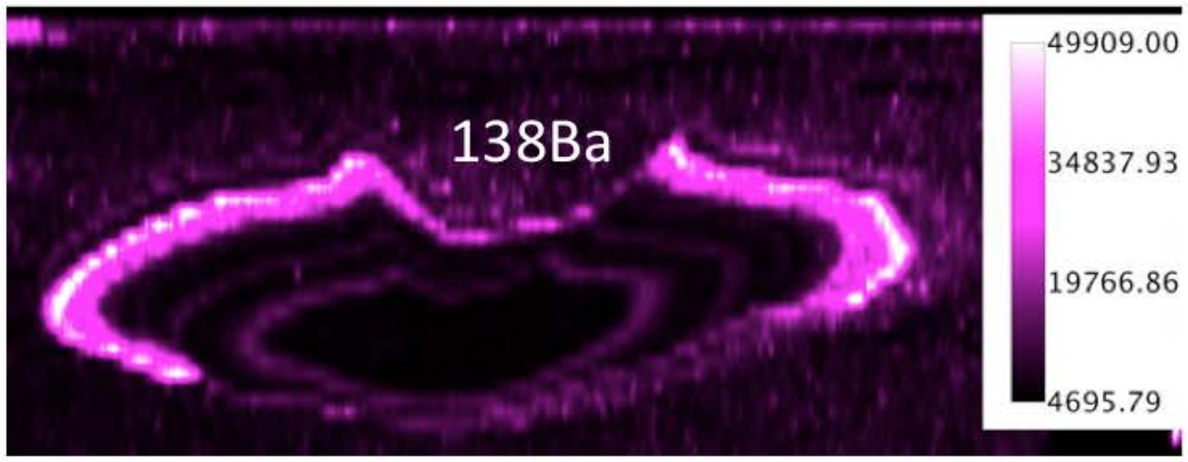
When images are required, the processed data are imported with ImageJ for easy handling.

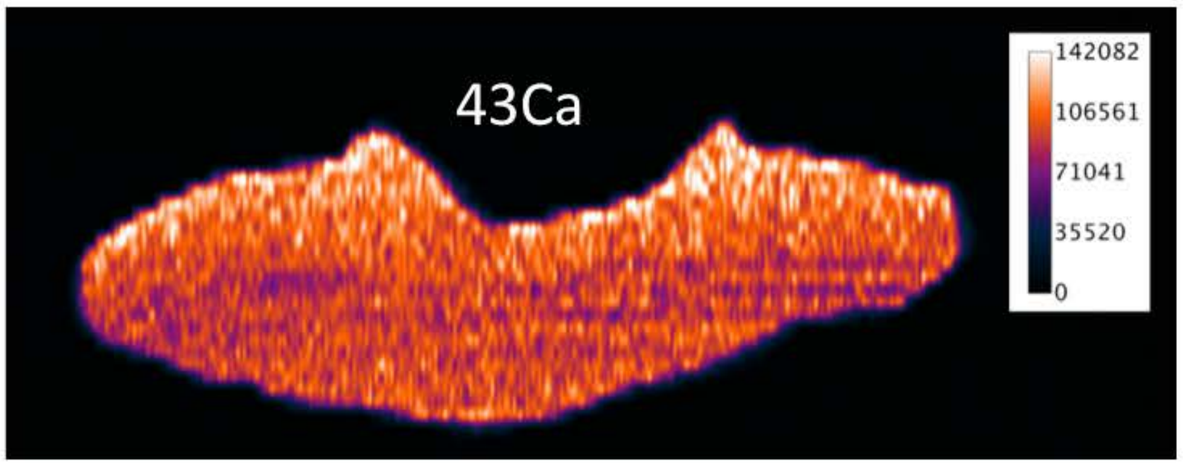
Otolith imaging

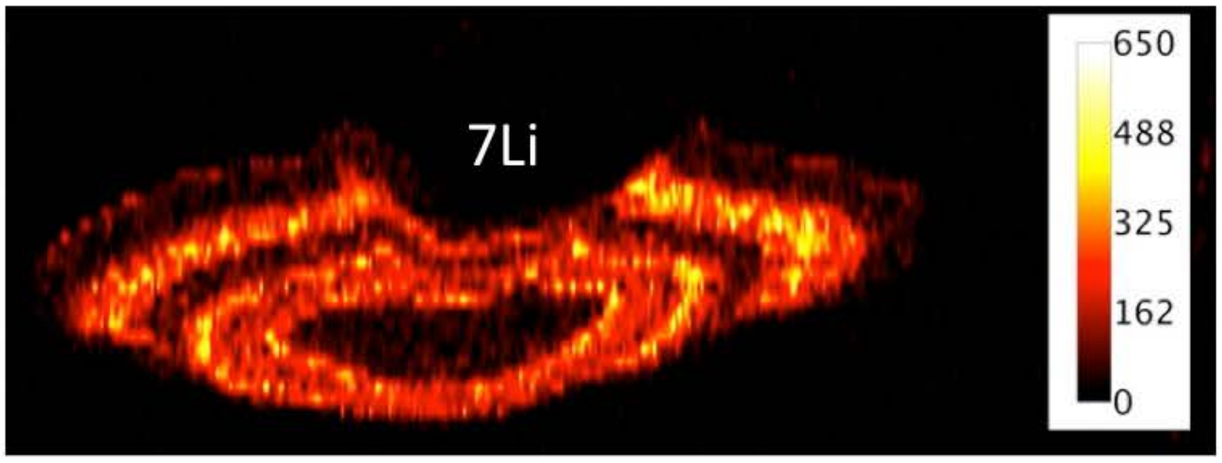
The sharp-blade shape allows real square pixels and better resolution.



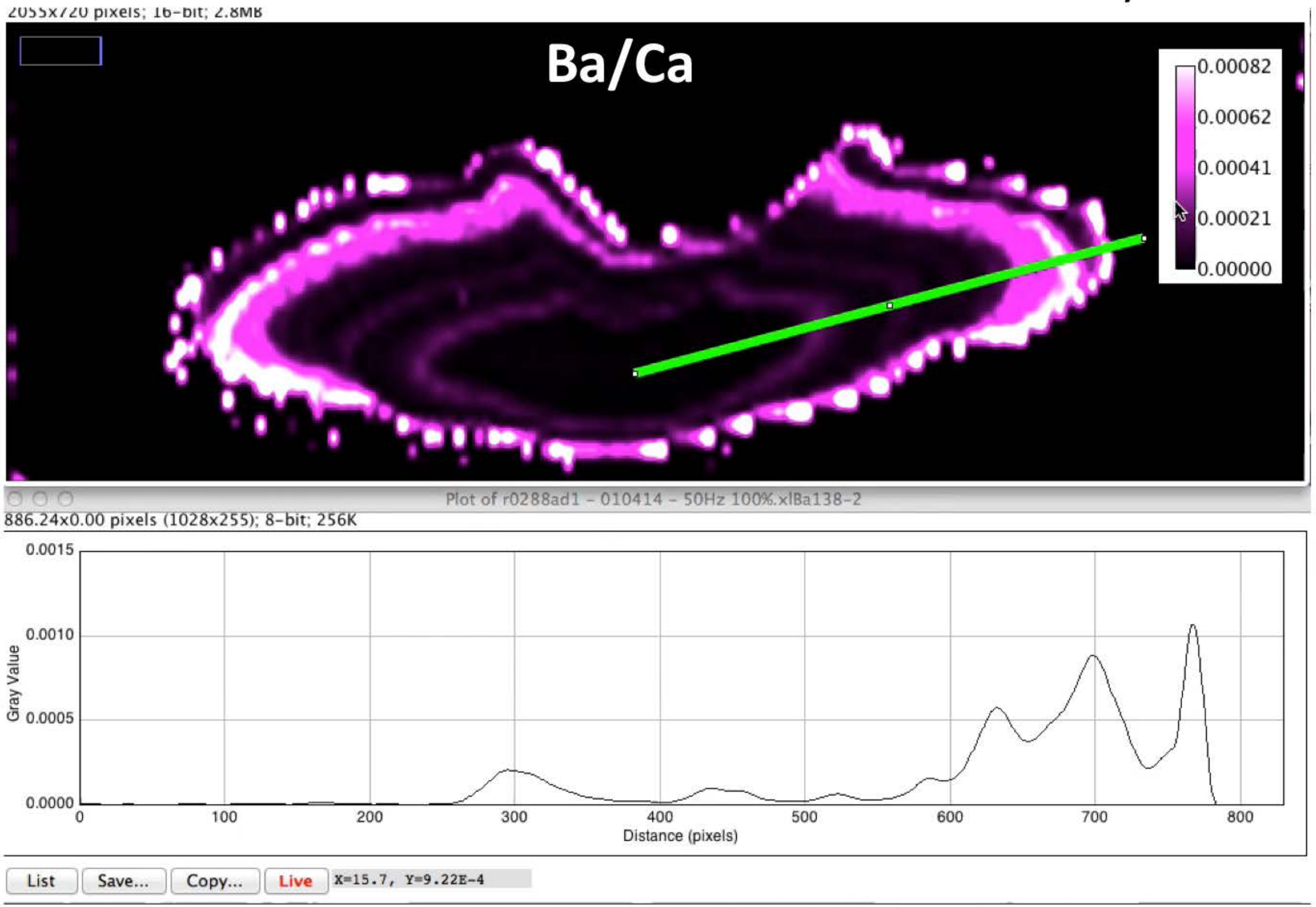
Once the image is acquired, select the desired axis for the plot profile







Otolith imaging as a decision tool to select the best ablation scan direction for routine analysis



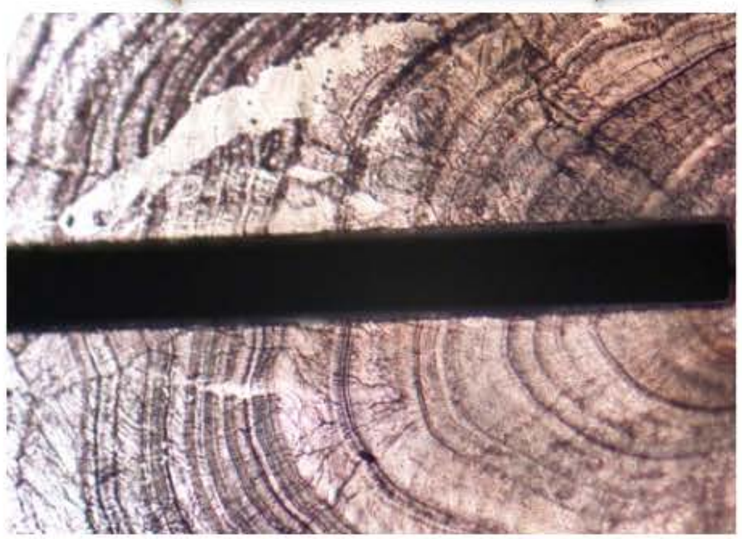
FsLA- 2D-SF-ICPMS : Simultaneous isotopic and trace element information

LAMBDA 3
360 Fs
1Hz-100 000 Hz
257 nm

Using the same laser trace....

Element XR (Jet Interface)

- High sensitivity (HRICPMS)

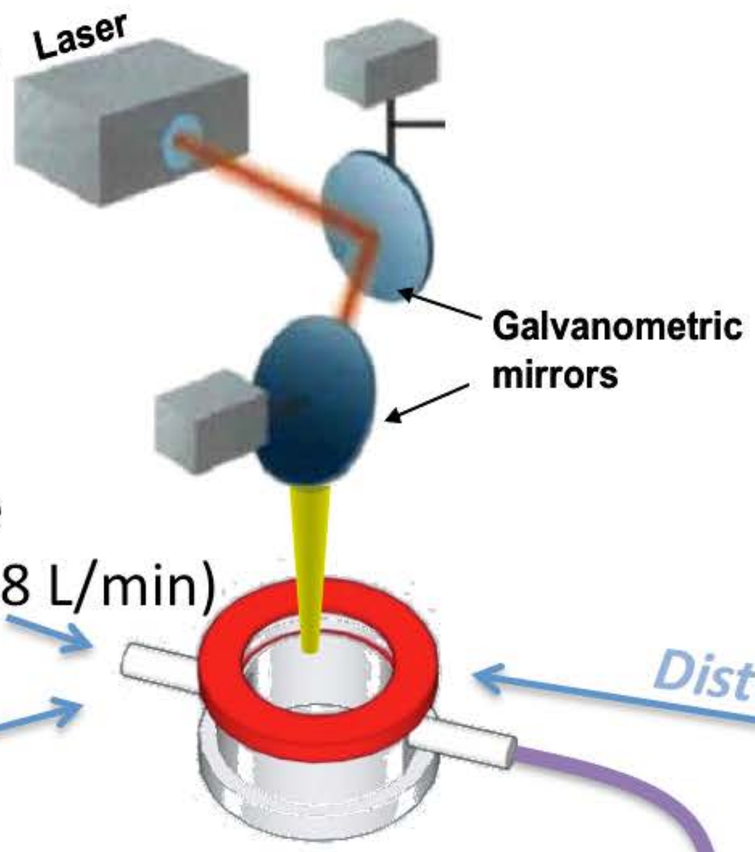


Nu Plasma HR

High isotopic precision (MCICPMS)

FsLA- 2D-SF-ICPMS : Simultaneous isotopic and trace element information

IR-Vis-Uv Fs Laser



- gas flow rate tuning
- split adjustment
- Plasma viscosity
- + and other parameters

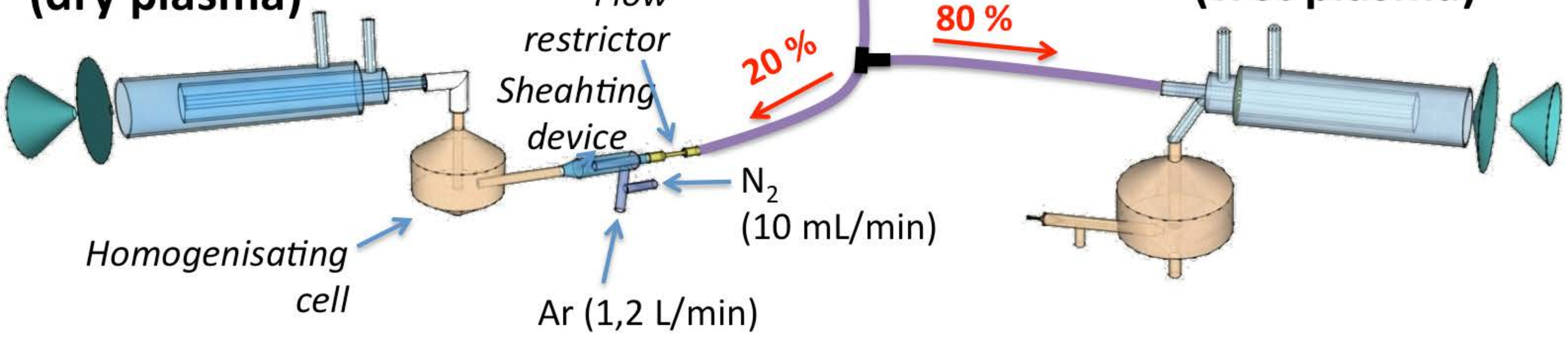
- Stability
- Sensitivity
- Accuracy

Distance : 2 m

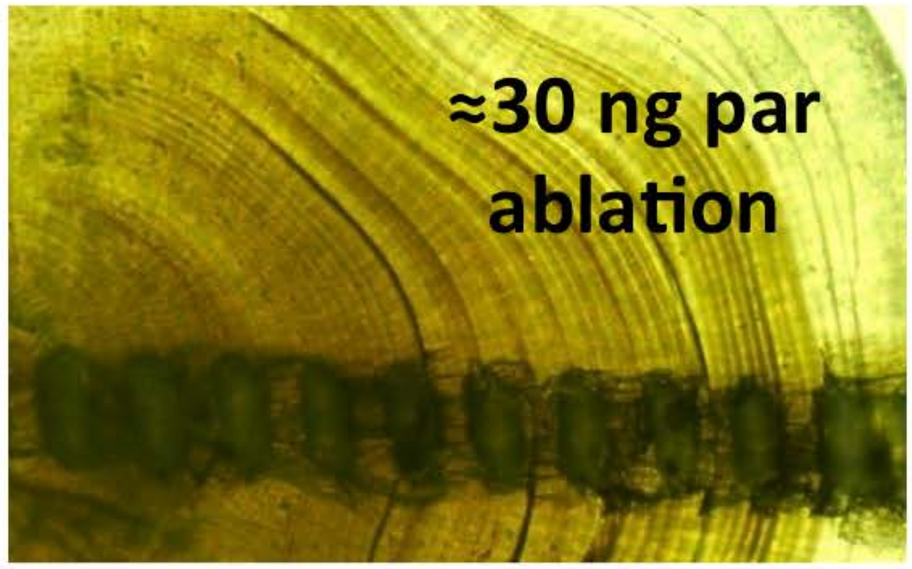
Distance : 10 m

Jet-HR-ICPMS (dry plasma)

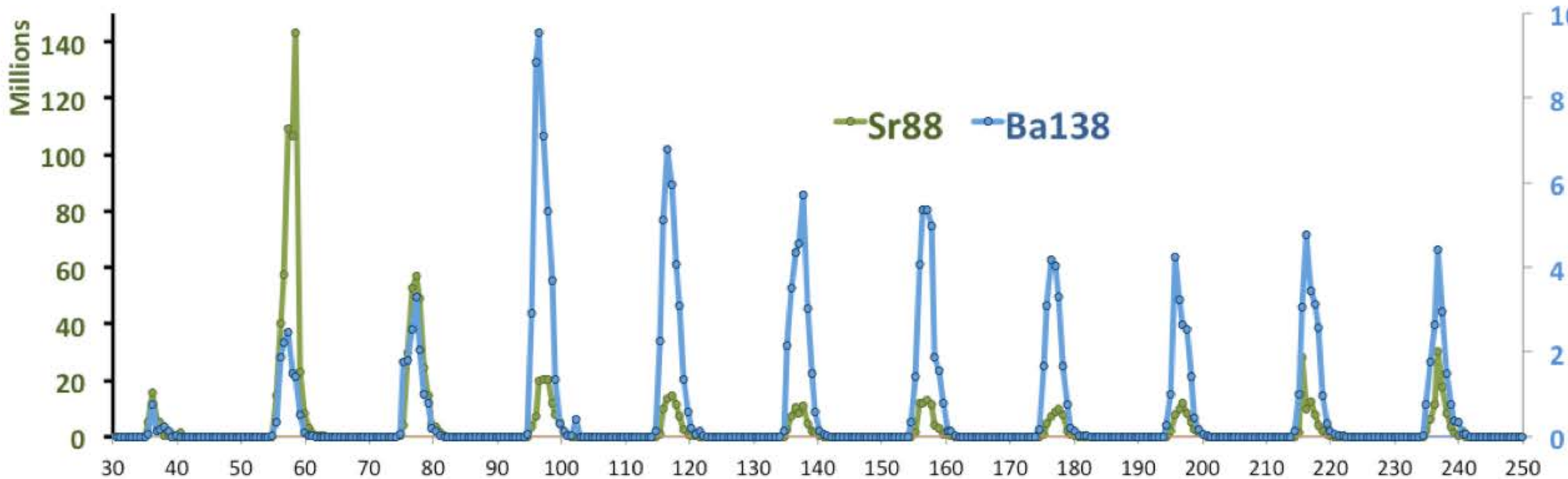
MC-ICPMS (wet plasma)



FsLA- 2D-SF-ICPMS :
Simultaneous isotopic and trace element information

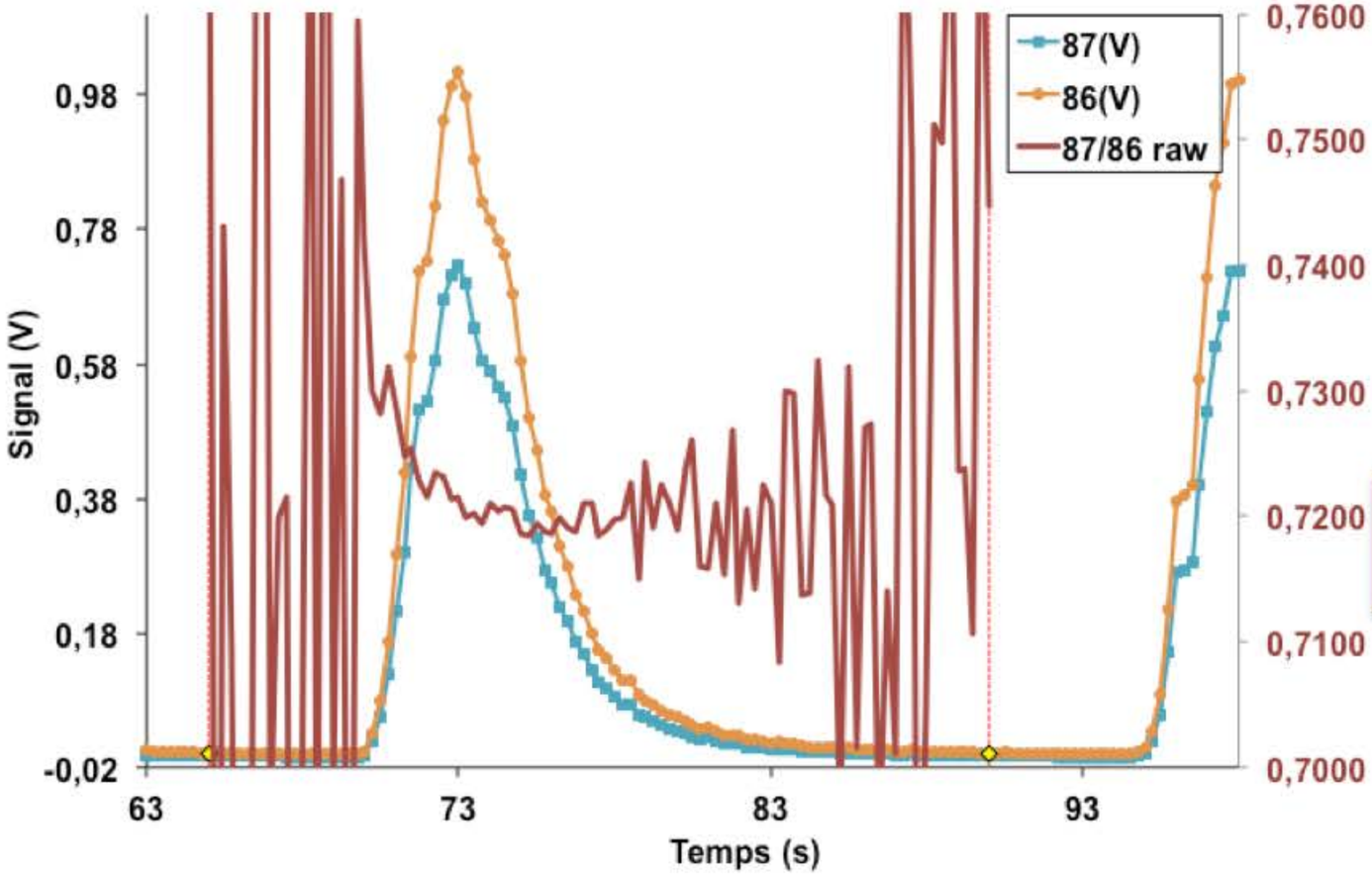


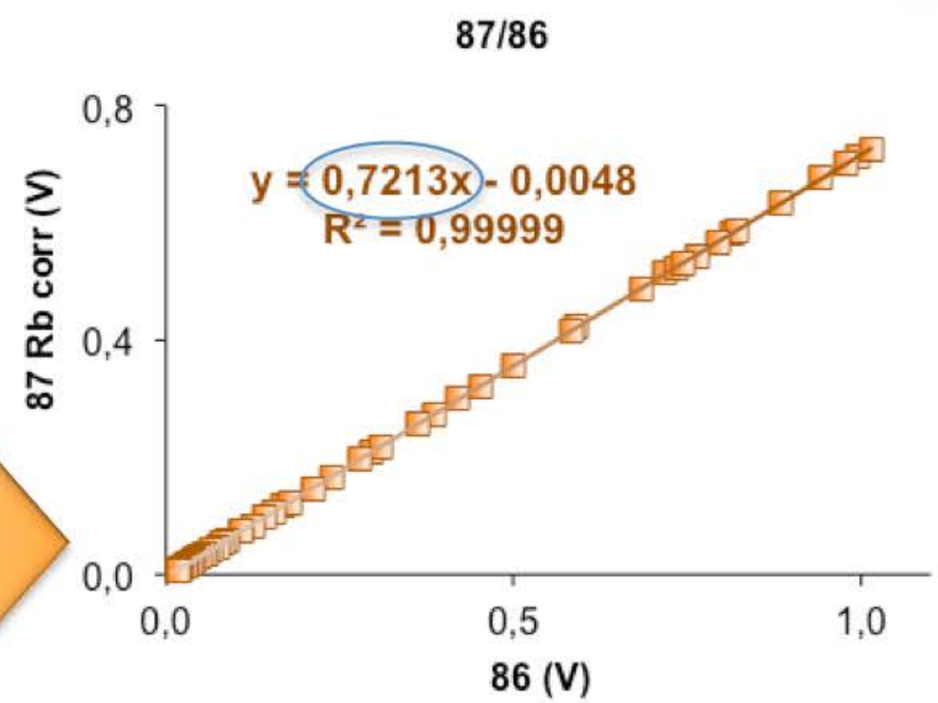
MC-ICPMS

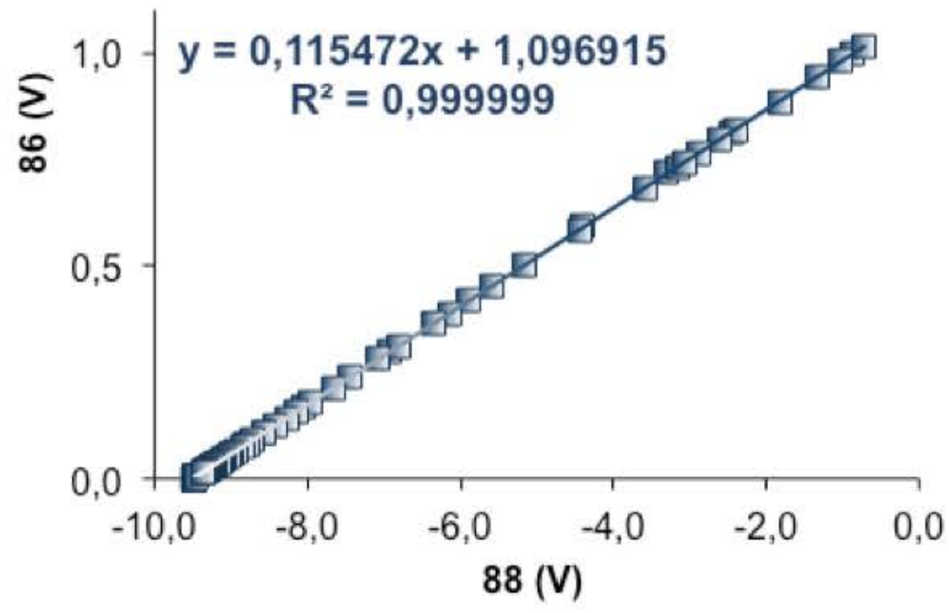


Jet HR-ICPMS

Isotopic data reduction for fast transient signal using an innovative Linear Regression Slope approach







- ❑ Very easy
- ❑ Natural weigthing of the statistic
- ❑ precision improved by x 10 (minimum)
- ❑ mass bias correction using 88Sr/86Sr

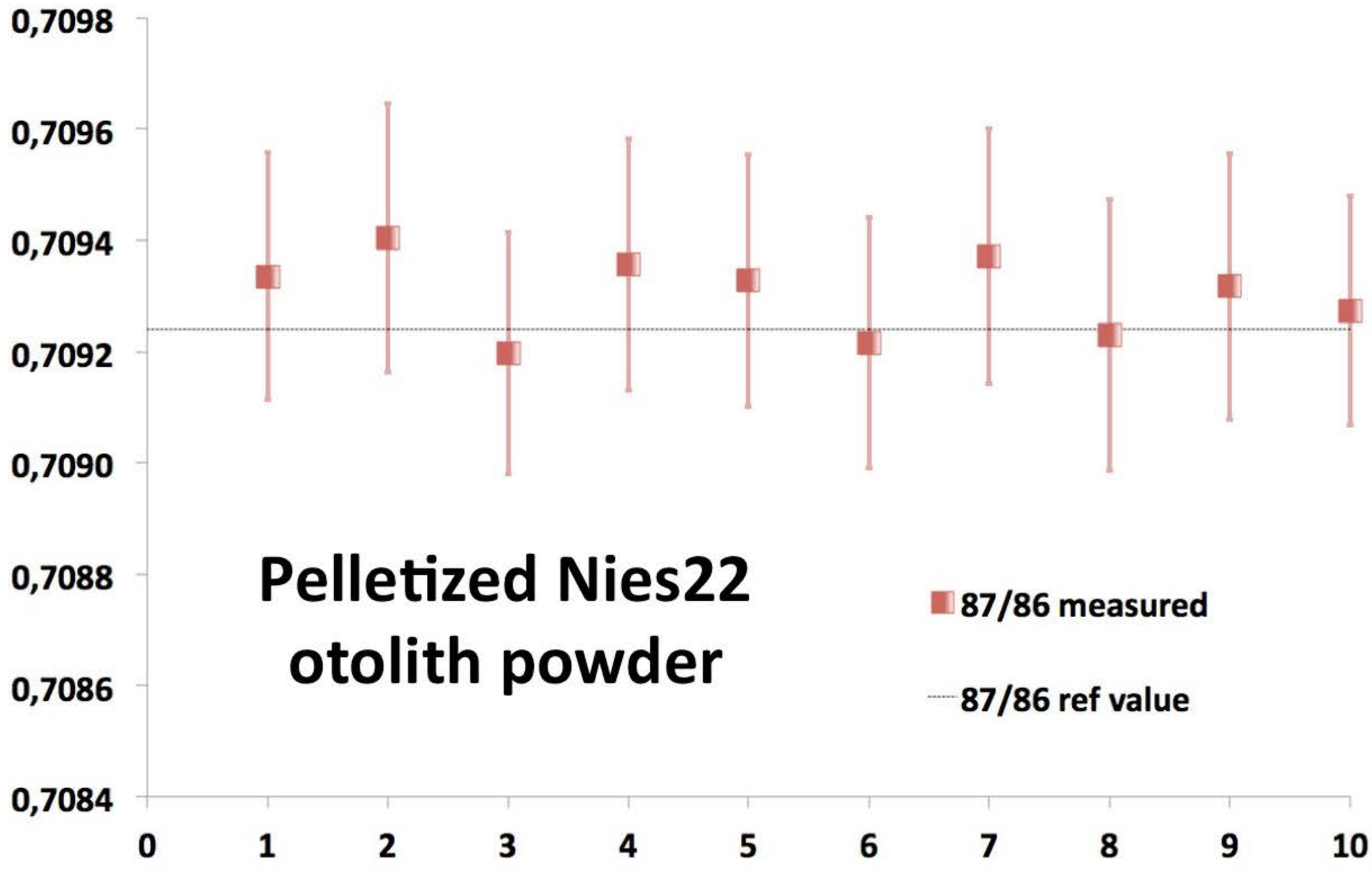
- *Fietzke et al.(2008), JAAS, Sr by LA/MCICPMS*
- *Epov et al.(2010), Anal. Chem: Hg by GC / MCICPMS*
- *Sanabria et al (2012), Anal.Chem; Pb by GC/MCICPMS*
- *Resano et al (2012), JAAS, Cu by LA/MCICPMS*

LCABIE

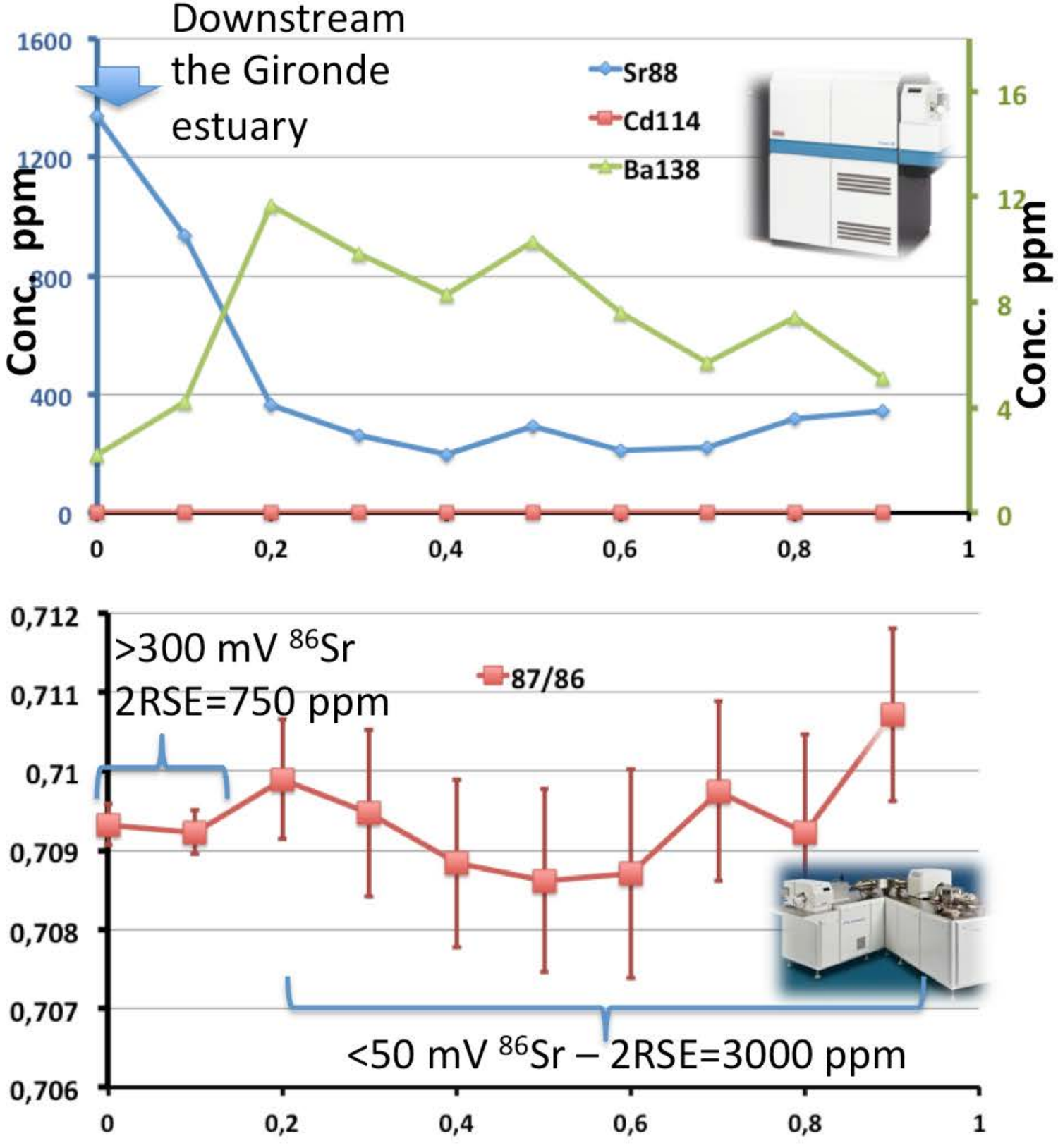
Precision on fast transient signal using the Linear Regression Slope approach

External Precision (2xRSD) n=10 : 200 ppm i.e. (0,02 %)

Internal precision (2xRSE): 600 ppm, (i.e. 0,06%)



FsLA- 2D-SF-ICPMS : Simultaneous isotopic and trace element information



Typical LODs with fsLA/Jet-HRICPMS

Sr =40 ppb *i.e.* ***1,2 femtograms***

Ba = 6 ppb *i.e.* ***180 attograms***

Cd = 4 ppb *i.e.* ***120 attograms***

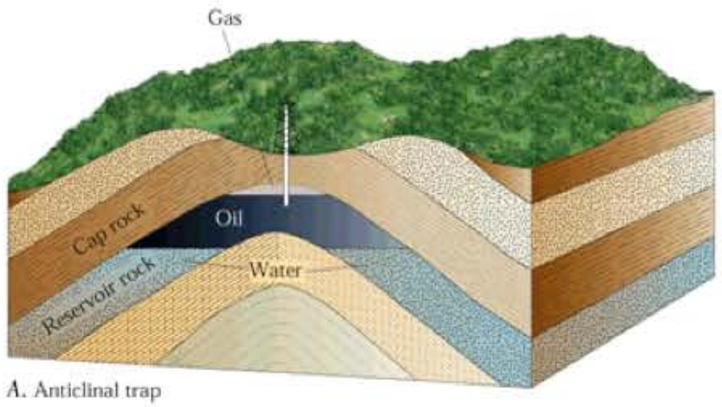
Versatile approach with complementary information. Relevant when some geochemical signatures are not significantly pronounced (here 87/86Sr)

Application of the virtual beam shaping to crude oil

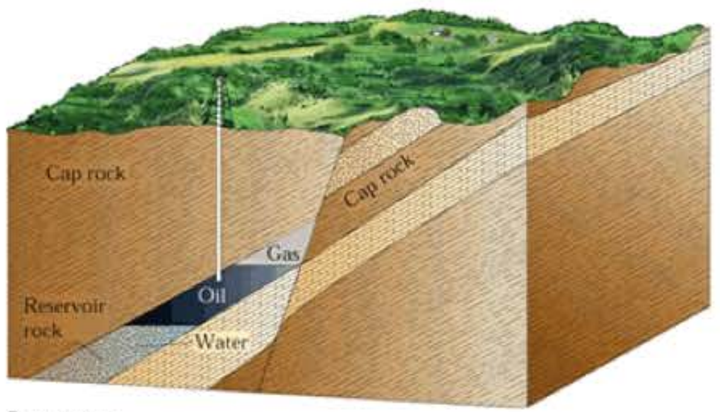
Direct anaysis of trace metals in petroleum product

Better understanding in petroleum reservoir => upstream (Exploration).

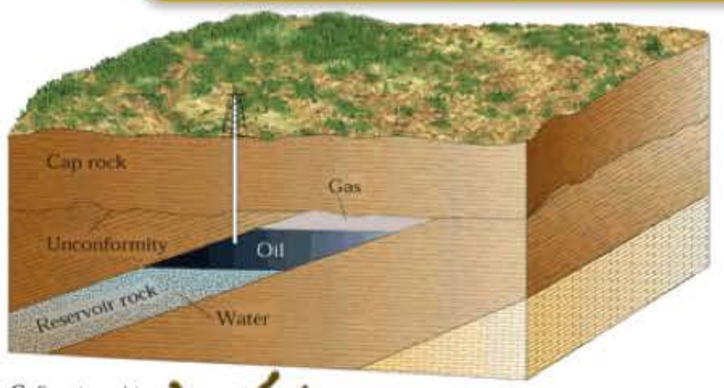
Geochemistry



A. Anticlinal trap



B. Fault trap



C. Stratigraphic trap

- **Oil-Oil correlation**
- **Oil-source rock correlation**
- **Deposits conditions**
- **Oil maturity**
- **Oil migration**
- **Degrees of biodegradation**

Analytical challenge

Organic product analysis still not easy in ICPMS :

- high sample dilution (crude oil)
- O2 feeding
- Mineralisation

Trace element analysis in crude oil by FsLA- ICPMS :

Laser Ablation

- **Direct analysis**

- **Very limited sample preparation**

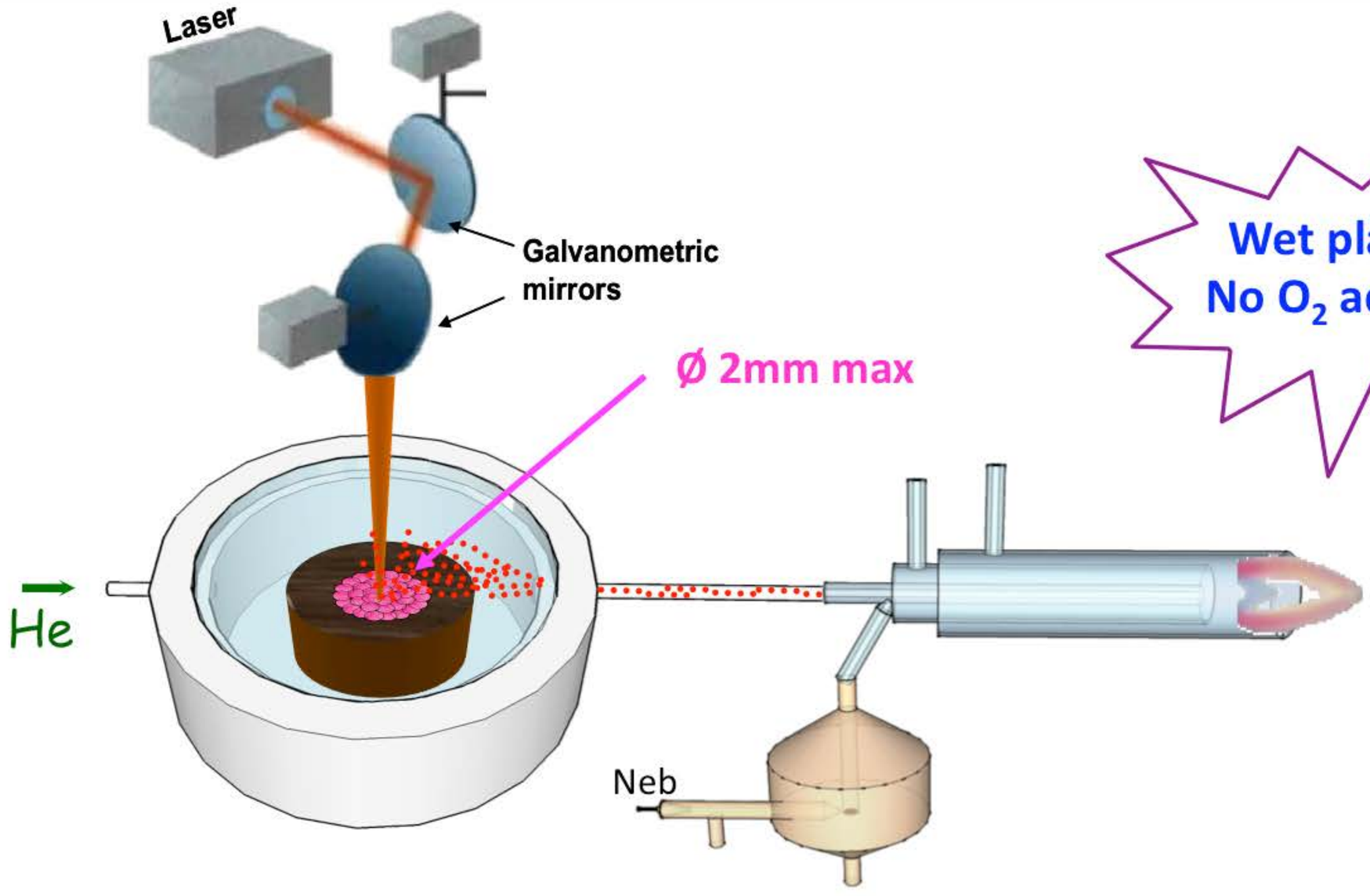
- **No sample dilution**

- **Low organic sample introduction (~20 µg/min)**
  ⇒ better plasma tolerance
  ⇒ No need for oxygen feeding

- **Fast analysis (< 2 min compared to 20 min in conventional nebulisation)**

High repetition rate FsLA/ ICPMS coupling

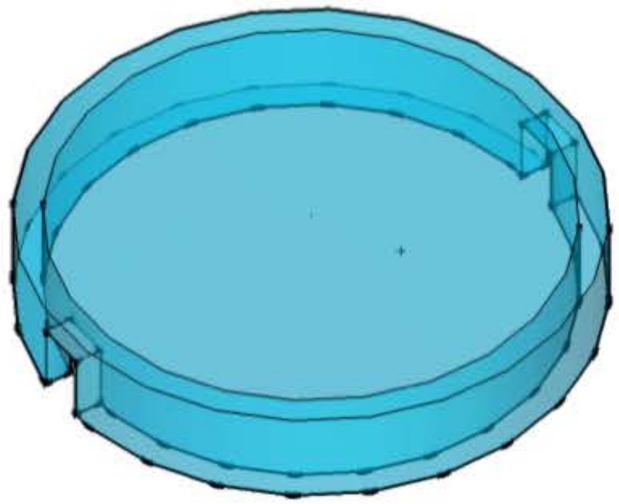
Trace element analysis in crude oil by FsLA- ICPMS :

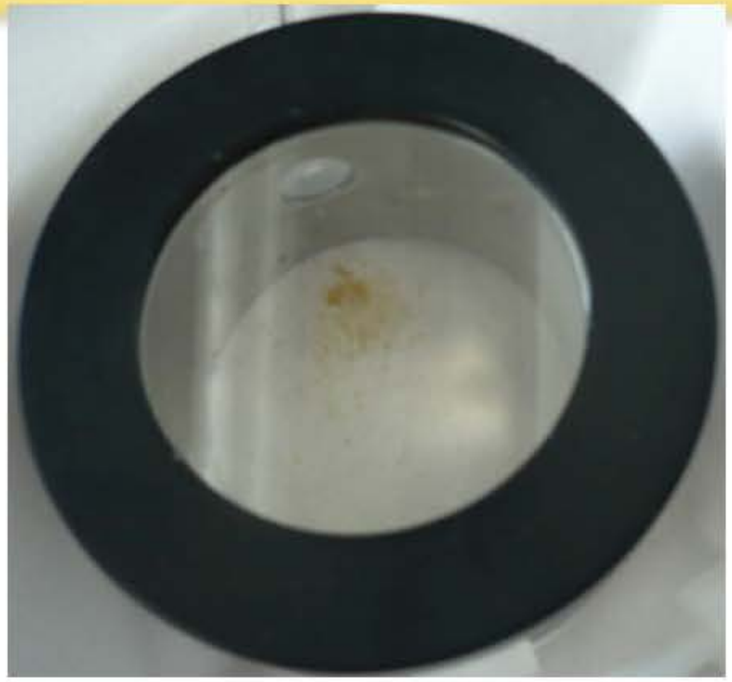


- **Wavelength : 1 030 nm,**
- **Pulse duration : 360 fs,**
- **17 µm laser beam**
- **Repetition rate : up to 10 000 Hz**
- **Fast 2D laser ablation trajectories (up to 280 mm.s^{-1})**

} High sensitivity

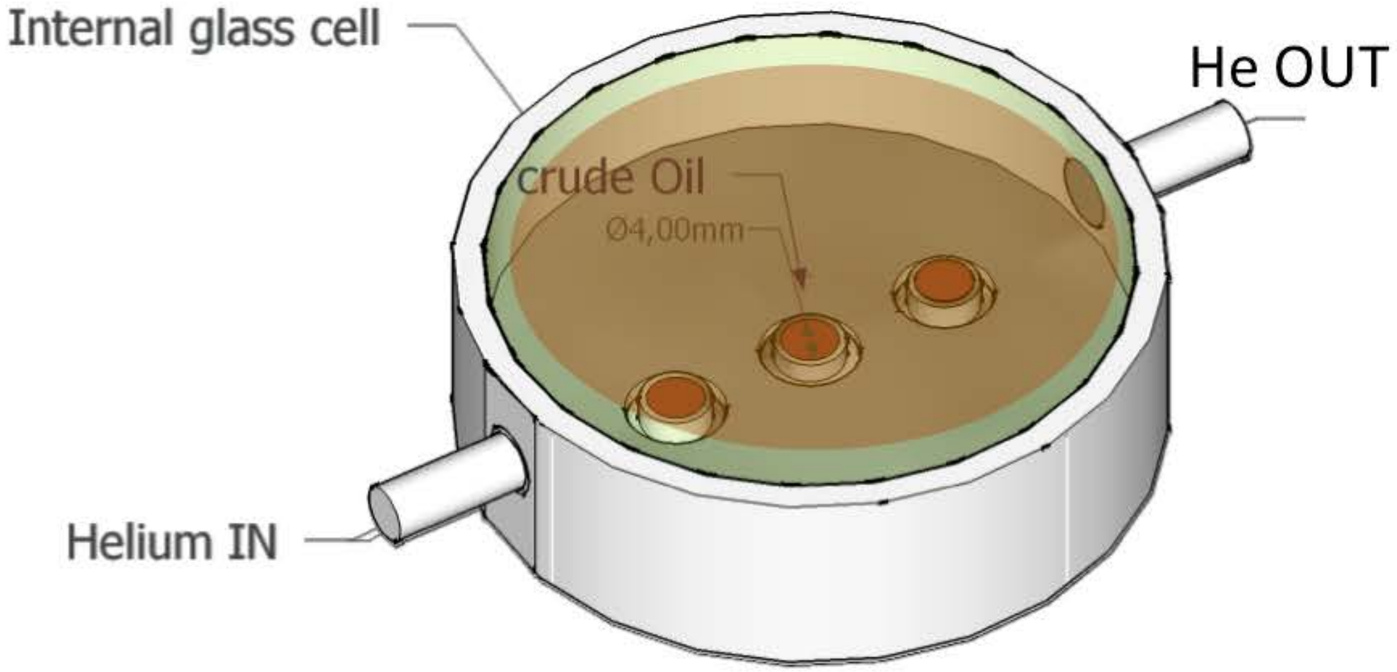
Trace element analysis in crude oil by FsLA- ICPMS :





Substantial splashing effects:

⇒ Contamination
⇒ Cell window alteration
⇒ Objective alteration



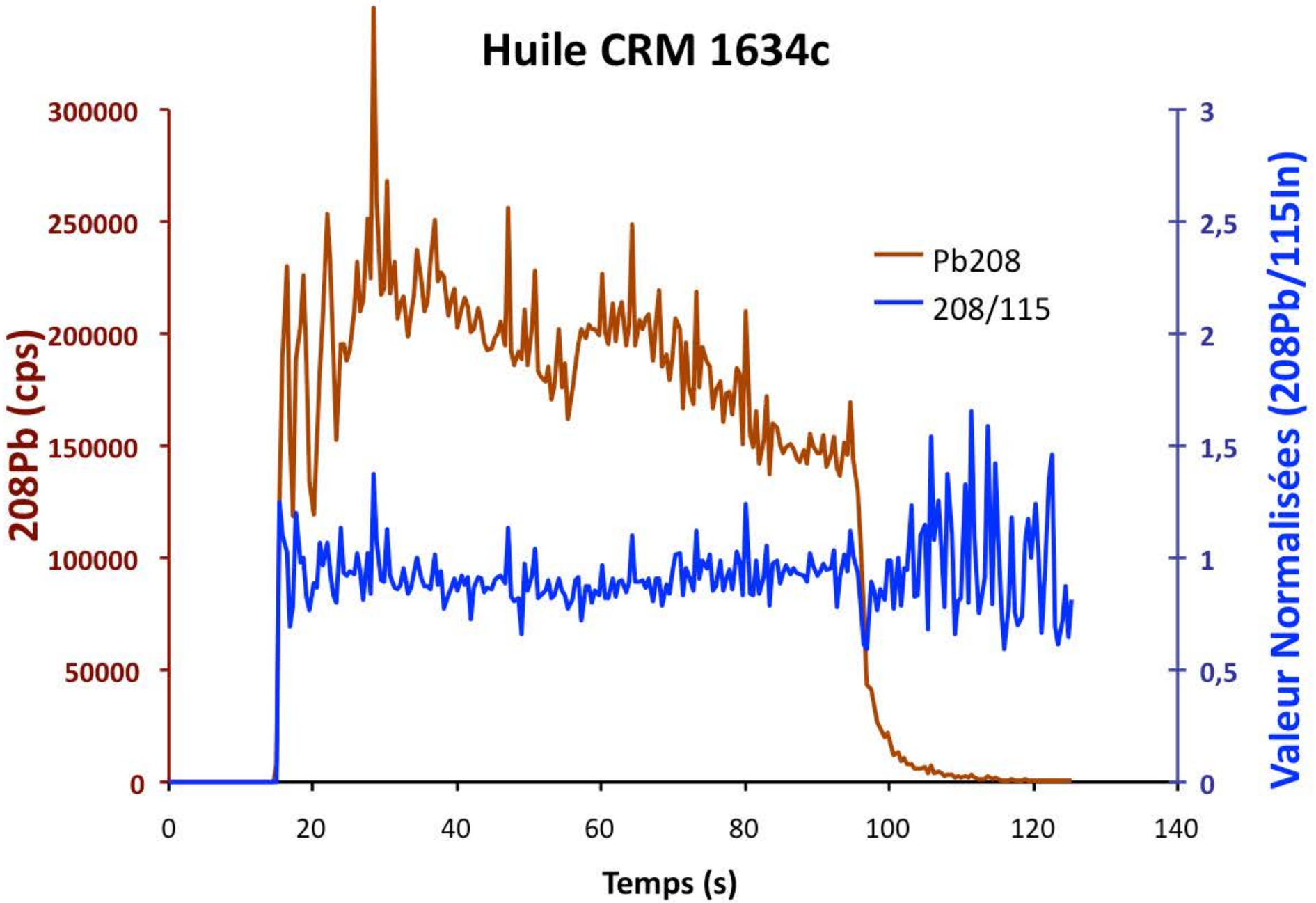
The internal cell **4 mm** above the samples acts as an impaction stage to:

⇒ Preserve the cell window
⇒ Stop splashes (large particles and droplets) just after ejection
⇒ Limit contamination

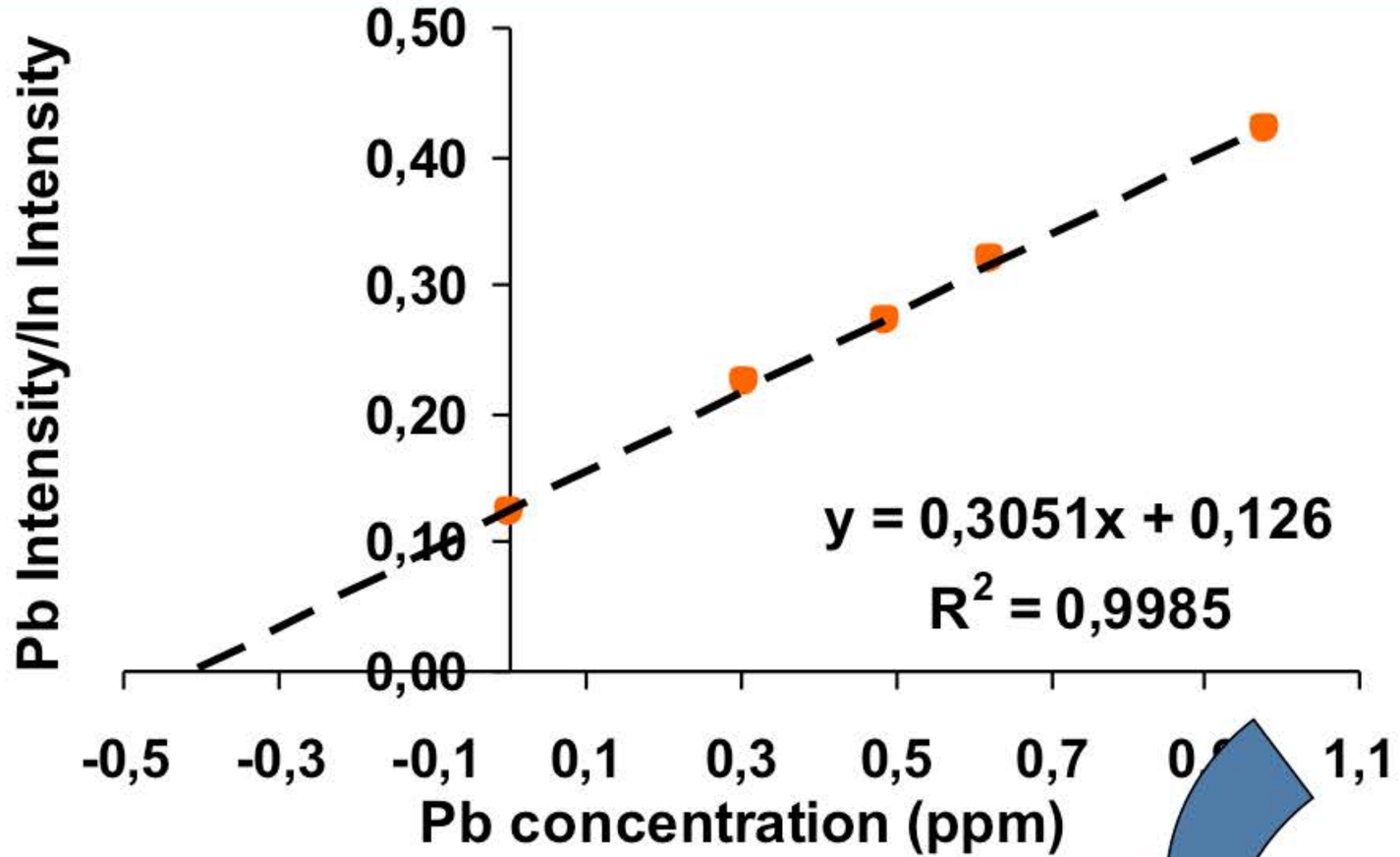
Trace element analysis in crude oil by FsLA- ICPMS :

Normalisation 115 In

200 ppb Pb



Trace element analysis in crude oil by FsLA- ICPMS :



	LOD (µg/g)
51 V	0.005
60 Ni	0.008
59 Co	0.001
75 As	0.007
98 Mo	0.002
208 Pb	0.0006

Optimal conditions: 1 KHz, 100 mm.s^{-1}, 30 J.cm^{-2}, => transport efficiency ~ 30 %

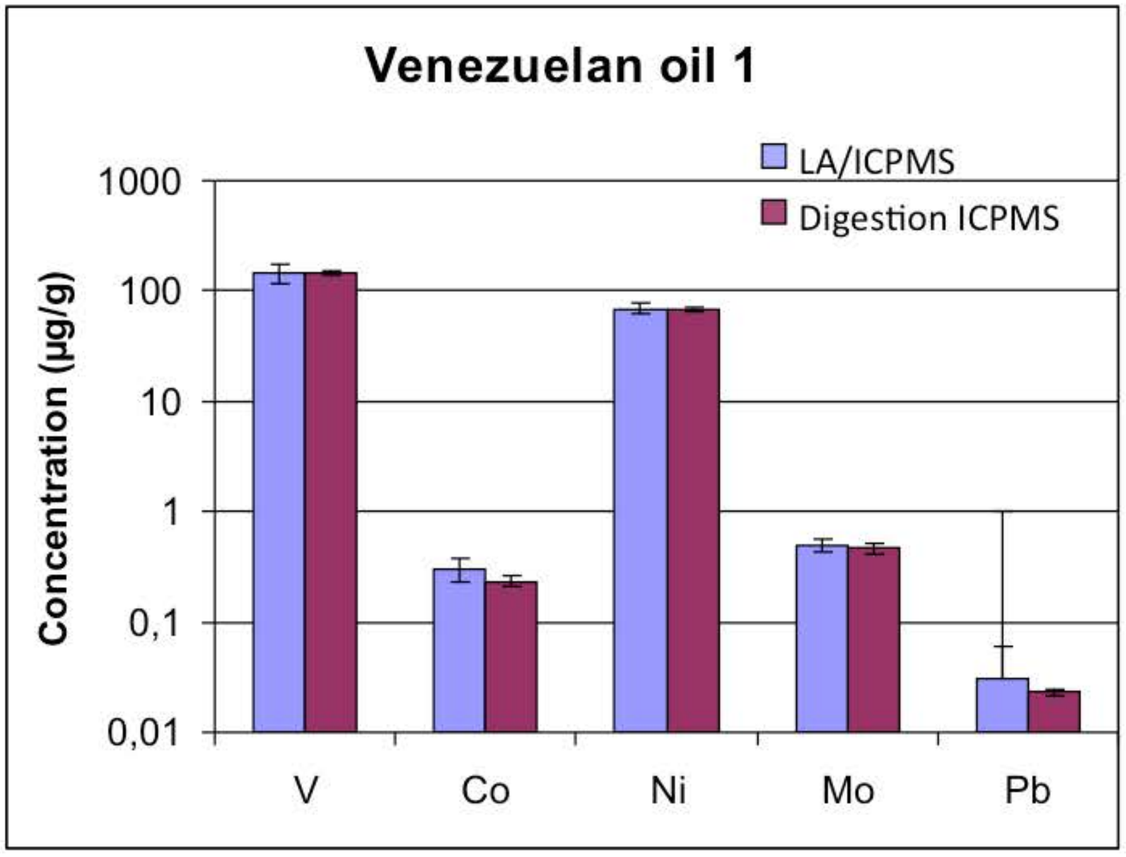
Sample preparation:

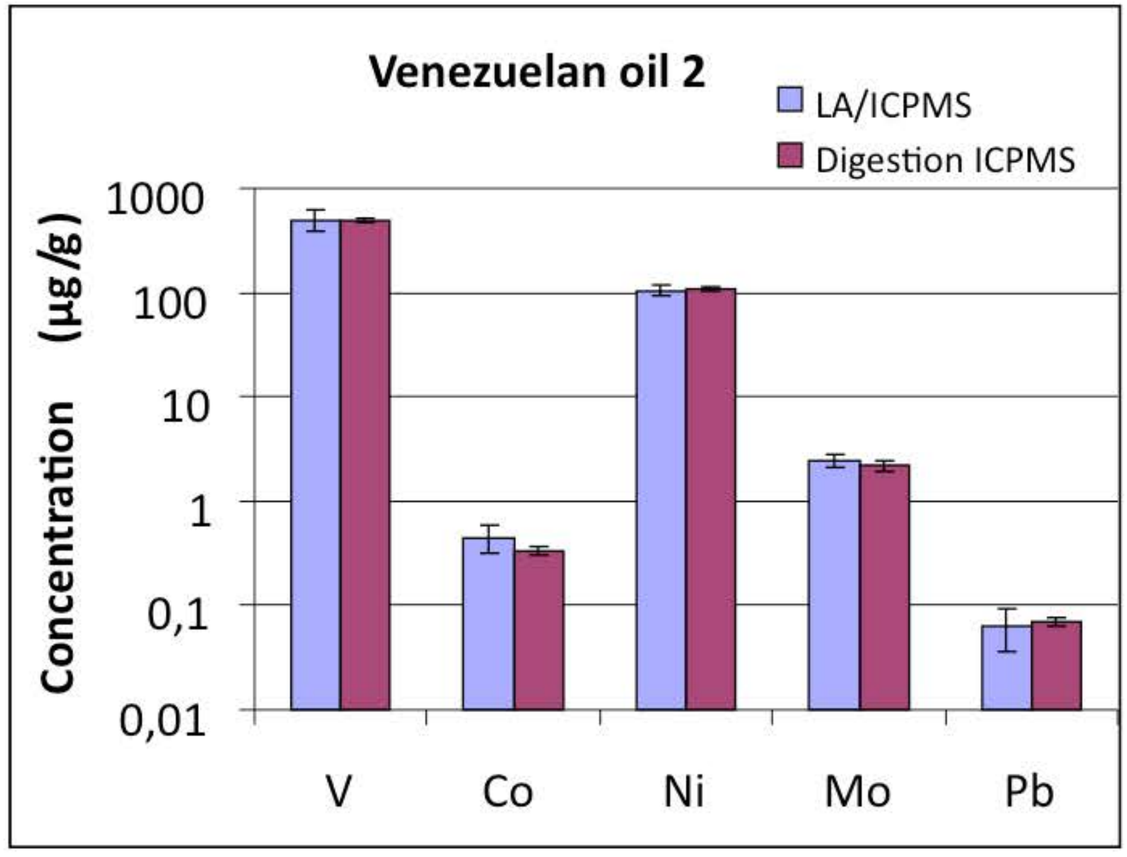
- **Indium** (internal standard) + Xylene (dilution 2 to 5)
- Evaporation under Nitrogen stream

Trace element analysis in crude oil by FsLA- ICPMS :

External calibration with NIST 1634c

=> Fast (2 min) and accurate…





In press in ABC

Forensic applications

Fighting against Wine counterfeiting

- Is this bottle counterfeited?
- Where is it from (country)?
- *Who did it?*

Trace element analysis in glass FsLA- ICPMS :

257 nm
Femtosecond laser
LAMBDA 3

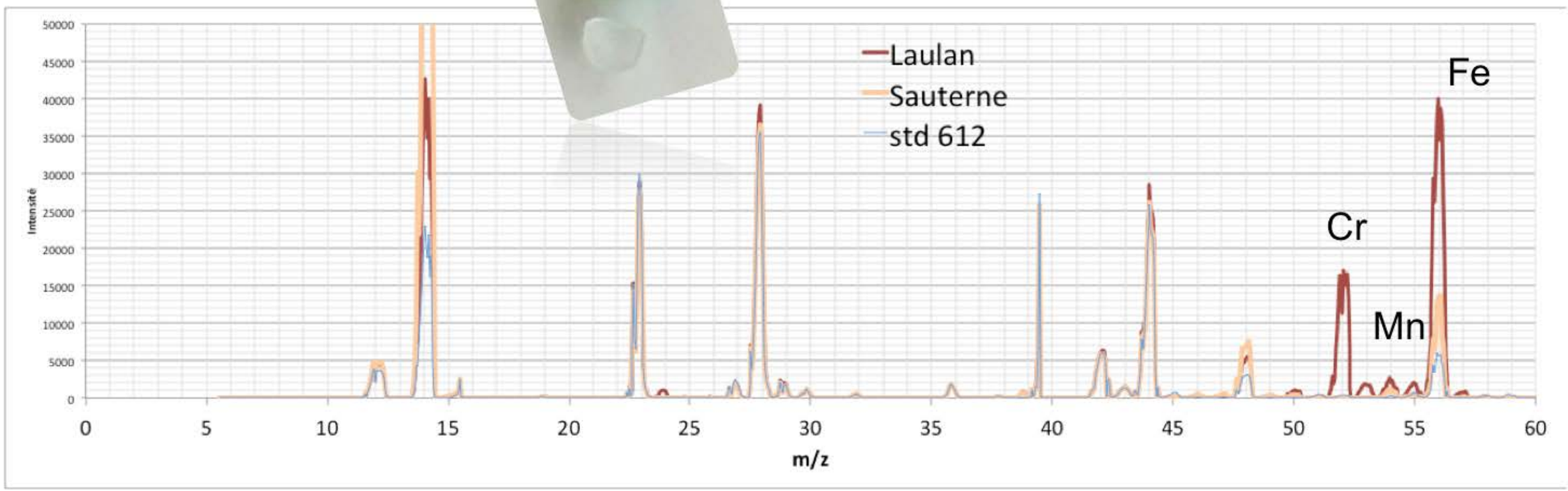
Ablation :
100 x 500 um

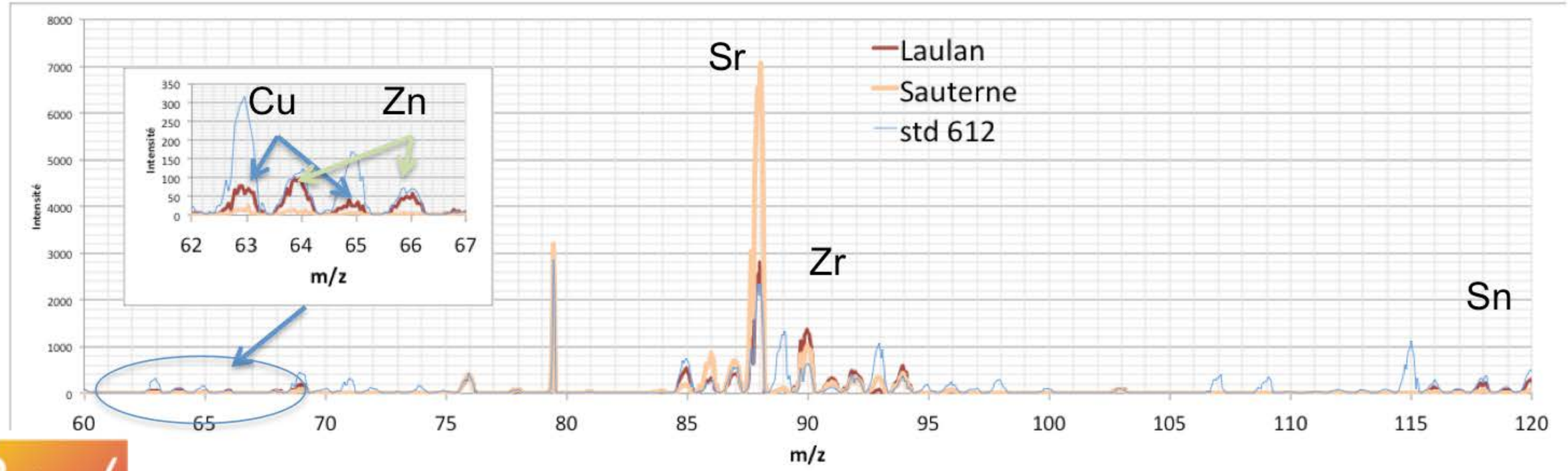
Calibration with NIST 612 (40 ppm)

Pamal
Femtosecond laser ablation

Trace element analysis in glass FsLA- ICPMS :

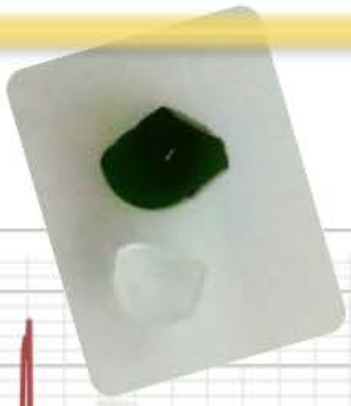
Semiquantitative analysis

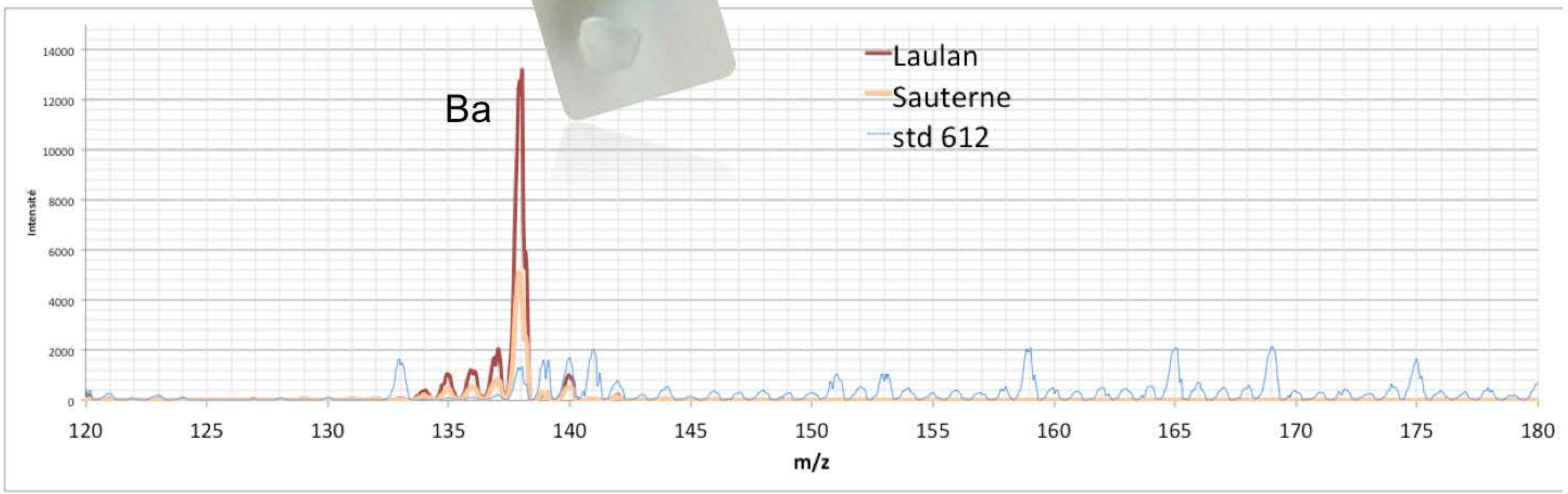


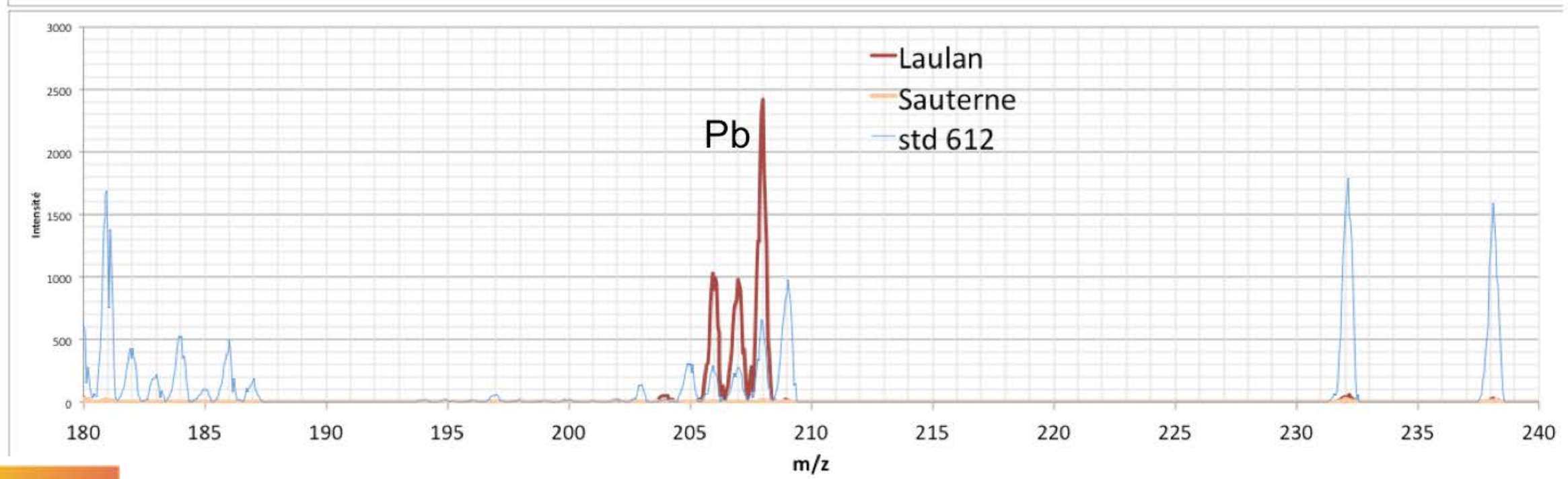


Pamal
Femtosecond laser ablation

Trace element analysis in glass FsLA- ICPMS :







Pamal
Femtosecond laser ablation

75 elements analysed by UVfs/HRICPMS

4 bottles of de Pauillac + 4 suspect bottles (Asia)
+ 1 copy of Pomerol (Asia)

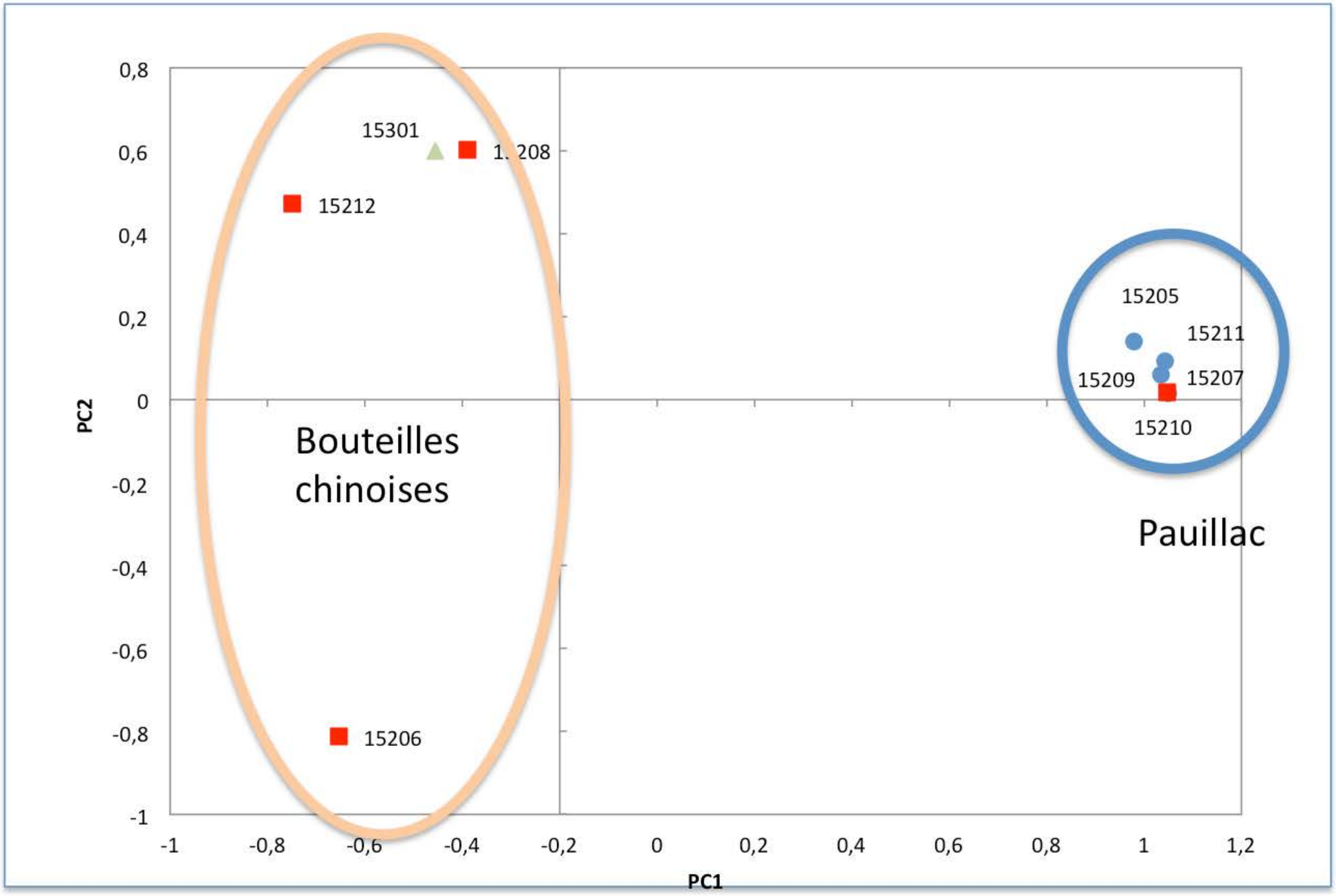
Li7	Ti47	**Rb85**	**Sn118**	Tb159	Ir193
Be9	V51	**Sr88**	**Sb121**	Dy163	Pt195
B11	Cr52	Y89	Te125	Ho165	Au197
Na23	Mn55	Zr90	I127	Er166	Hg202
Mg24	Fe56	**Nb93**	**Cs133**	Tm169	Tl205
Al27	Co59	Mo95	**Ba138**	Yb172	Pb208
Si28	Ni60	Mo98	La139	Lu175	Bi209
P31	Cu63	Ru101	**Ce140**	**Hf178**	Th232
S32	**Zn66**	Rh103	Pr141	Hf179	U238
Cl35	**Ga69**	Pd105	Nd146	**Ta181**	Pu239
K39	Ge72	Ag107	**Sm147**	**W182**	
Ca44	**As75**	**Cd111**	Eu153	Re185	
Sc45	Se78	**In115**	Gd157	Os189	

Very discriminating
Discriminating
Poorly discriminating

⇒ **LOD: 0,06 ng/g (Pr) – 2 ng/g (Pb) - 20 ng/g (Sn)** **all analyzed in medium resolution**
(so with only 10% transmission)

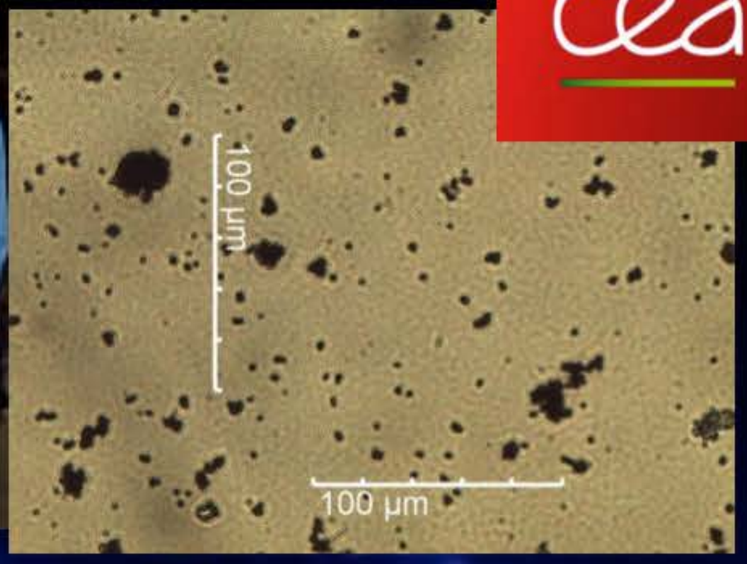
=> 20 discriminating elements with 9 highly discriminating

Unambiguous authentification using PCA



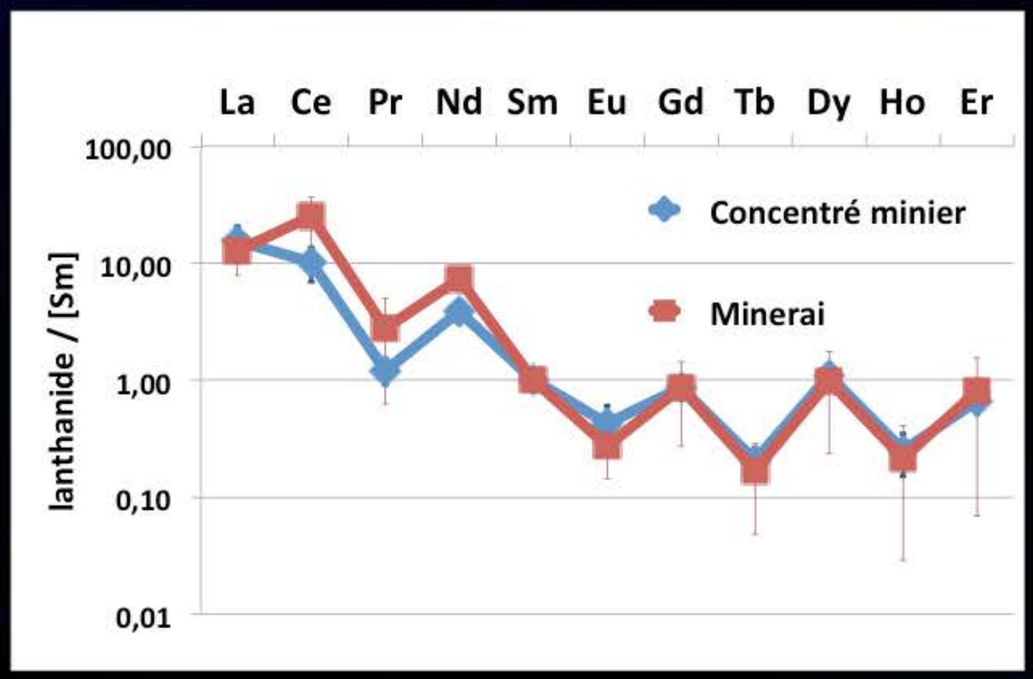
Le millésime 2006 suspect est en fait un vrai Pauillac

Forensic sciences at the particle size

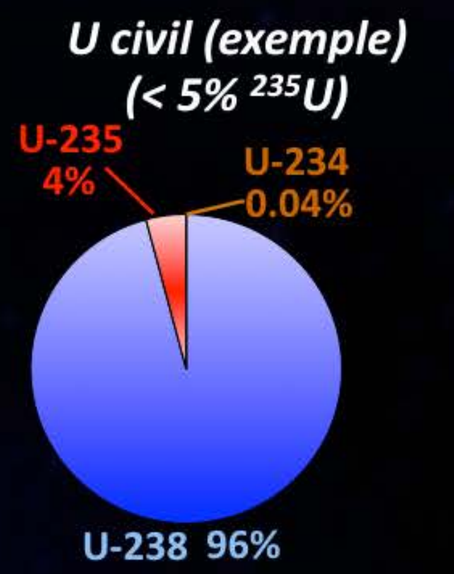


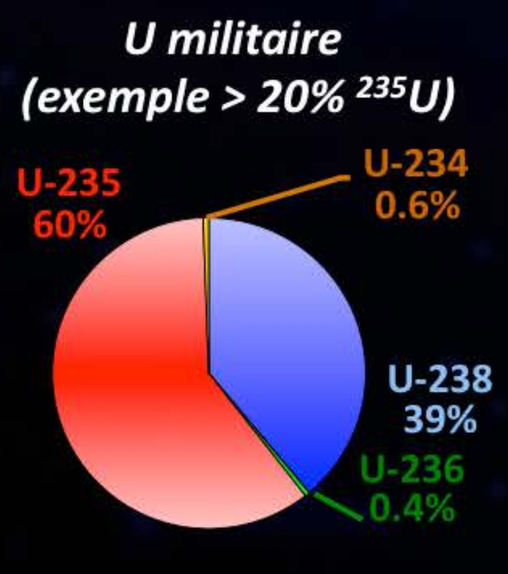
particles of few nanograms => detection of few pico, femto and even attograms

ORIGIN



USE





Uranium isotopic composition of micrometric particles

In the framework of the Non Proliferation Treaty (NPT, 1968), whose aim is to avoid spreading of nuclear weapons, the ***International Atomic Energy Agency*** ***(IAEA)*** *is in charge of controlling the nuclear installations worldwide in the countries that established safeguard agreements with the IAEA (183 countries have signed the treaty, 50 operated nuclear facilities).*

IAEA

IRAK, 1991: due to the discover of a clandestine nuclear enrichment program **(not detected by regular inspections),** the IAEA became aware of the limitations of the controls previously carried out, only on **nuclear materials declared and accessible to the inspectors in declared facilities**.

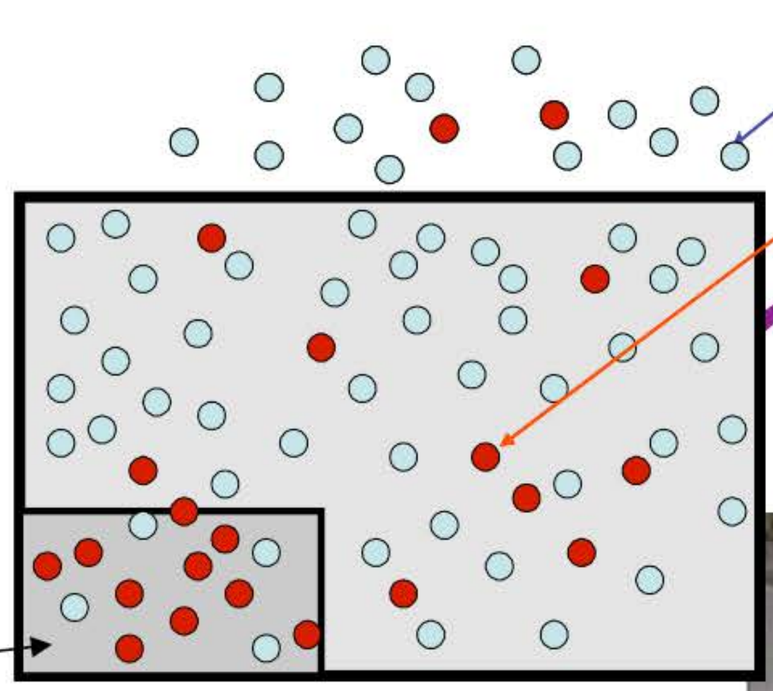
- Undeclared facilities => no control
- Undeclared nuclear material => not collected by inspectors

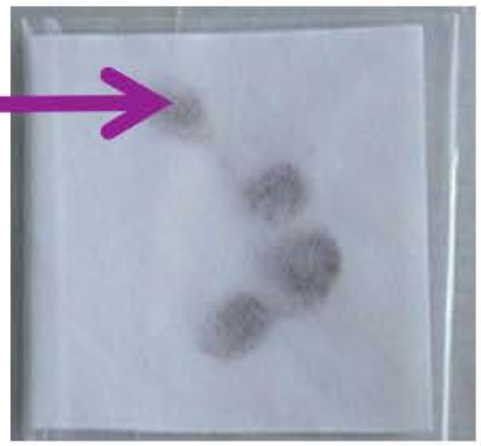
Urgent need to reinforce legal protocols and analytical methods

Uranium isotopic composition of micrometric particles

The challenge is to detect and characterize nuclear materials (uranium, plutonium) present in a nuclear facility, without access to these materials

Physico-chemical processes applied to a material, or even the displacement itself of a material release some very thin particles (< µm to few µm) that will spread in the nuclear facilities or around.

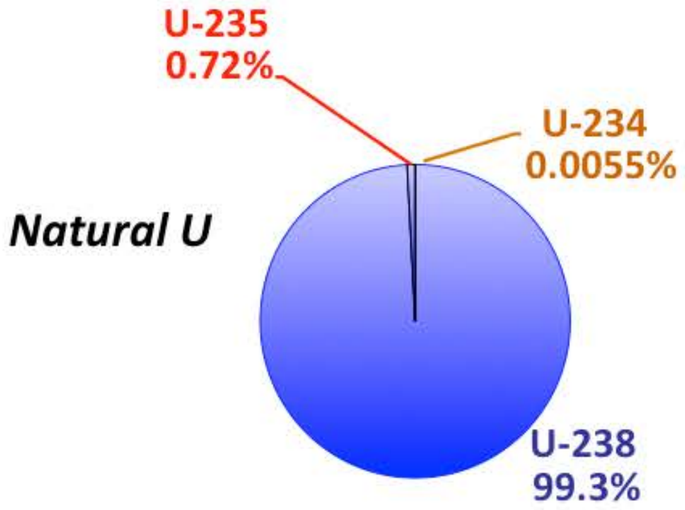




Cotton cloth (*swipe samples)*, used for collecting particles on surfaces (walls, tubings, etc…), and in the vicinity of the nuclear facilities.

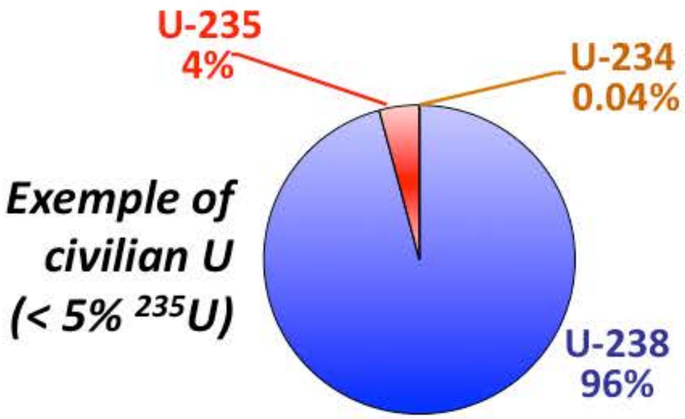
Uranium isotopic composition of micrometric particles

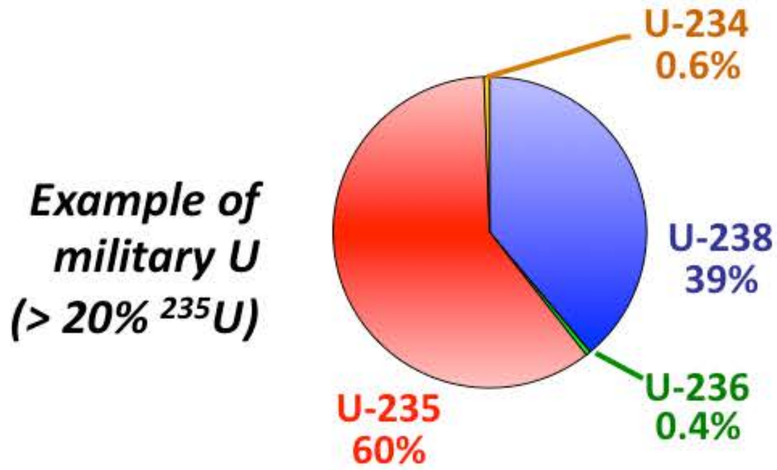
▸ **Aim**: determine the **use** (military, civilian, natural,….) and, if possible the **associated treatment** (irradiation, purification, enrichment process, …) and the **origin** of the nuclear material.



▸ Isotope ratios to discriminate between civilian and military use of the nuclear material :

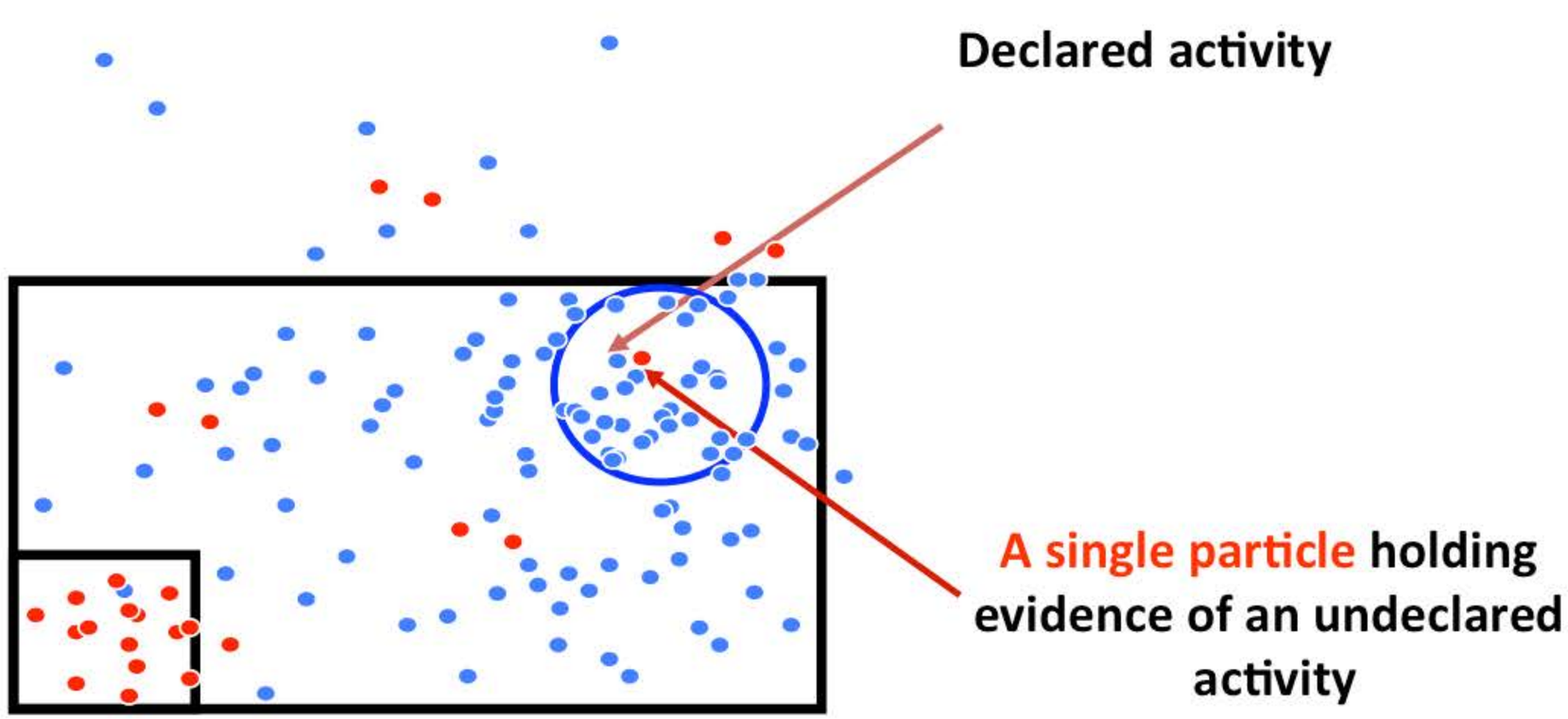
- $^{235}U/^{238}U$, $^{234}U/^{238}U$, $^{236}U/^{238}U$
- $^{240}Pu/^{239}Pu$ ($^{241}Pu/^{239}Pu$, $^{242}Pu/^{239}Pu$)





Uranium isotopic composition of micrometric particles

- The widespread method of "bulk analysis" (dissolution, chemical purification and isotopic analysis of the cotton cloth as a whole sample) provides an average isotopic composition of the particles and may allow detecting undeclared materials.
- However, this method is not efficient when the sample contain only one particle enriched in fissile ^{235}U isotope (or a very limited number of these particles) among a vast majority of particles coming from declared materials (for instance natural uranium or uranium depleted in ^{235}U).

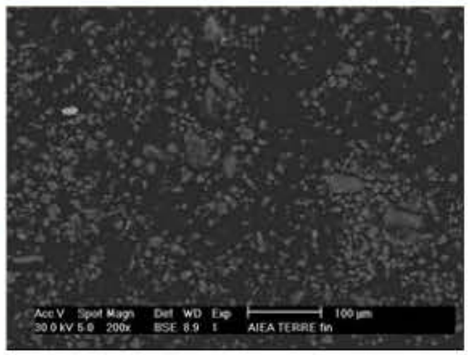


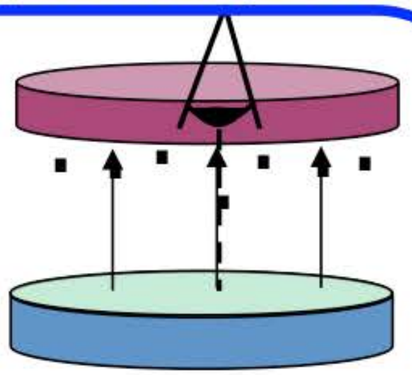
- **<u>Towards analysing isotopic signature of individual particles...</u>**

Uranium isotopic composition of particles (CEA, DAM)

1 - Particles extraction and deposition on disks

2 - Localization and selection of the most pertinent particles





Scanning Electron Microscopy
Detection and localization of the "largest" particles (∅ ≥ 1 µm)

Fission tracks : detection and localization of the high ^{235}U content-particles

3 - Isotopic analysis of U isotopes

SIMS

Particles are directly analyzed

☹ Not selective for ^{235}U enriched-particles

☺ **4 analysis per hour**

TIMS

Micro-sampling of the particles, deposition on a Re filament and introduction in the TIMS source

☺ Selective for ^{235}U enriched-particles

☹ **1 analyses per hour**

LA-ICPMS

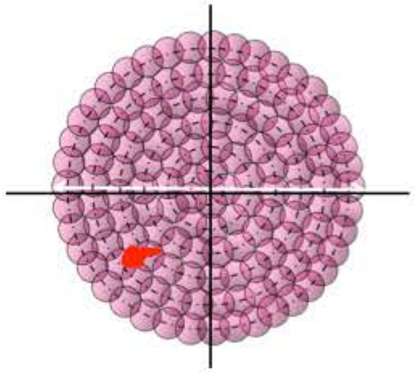
Particles are directly analysed

Potential??

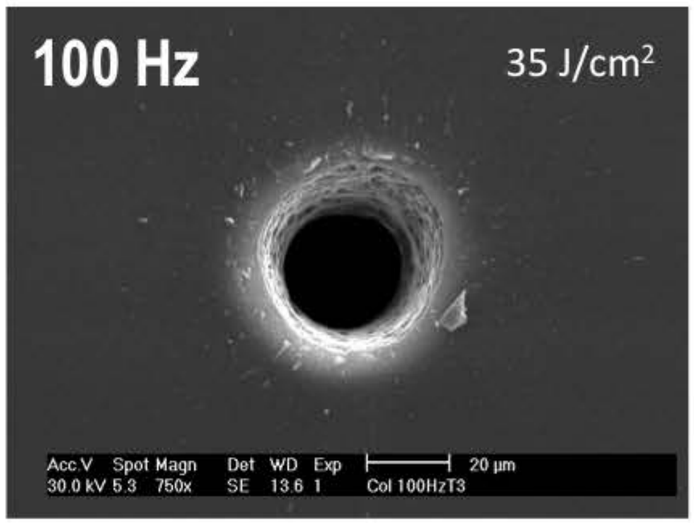
Uranium isotopic composition of micrometric particles

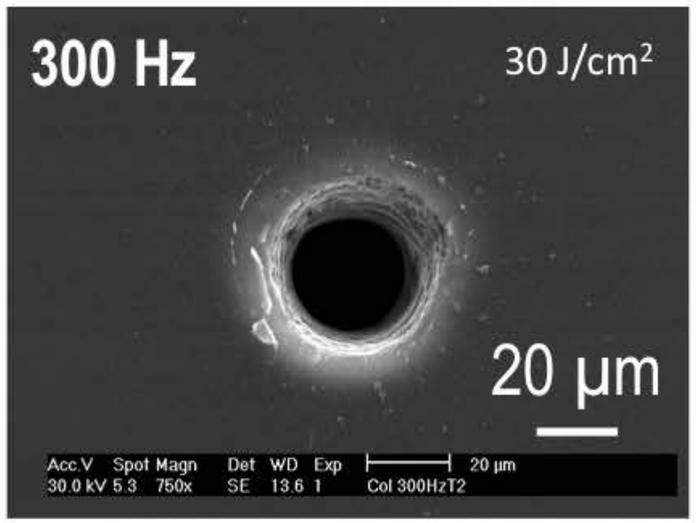
fsLA/ICPMS

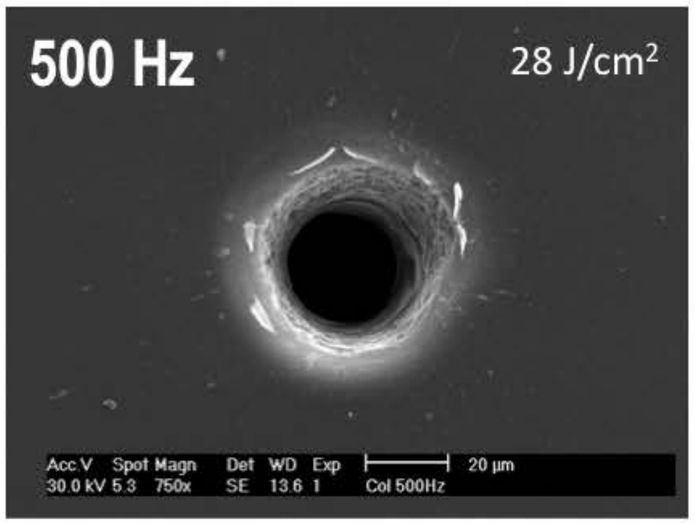
- Particles coordinates known at ± 5-10µm
- Particles analysed : < 3 µm diameter

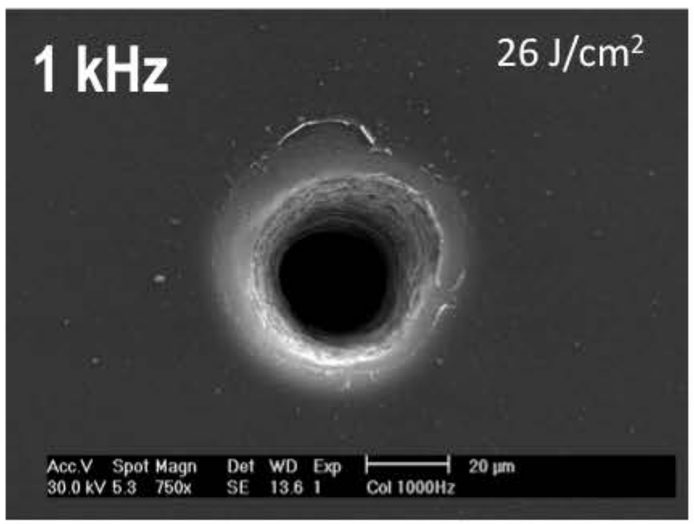


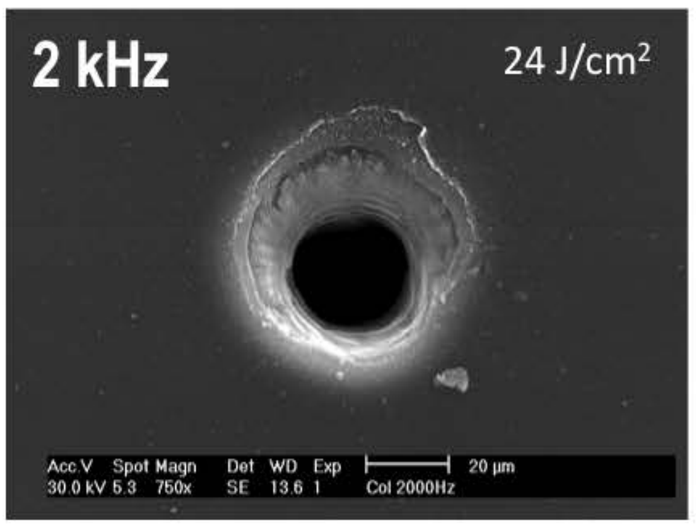
Crater of 40 µm diameter to make sure to ablate the particles of interest

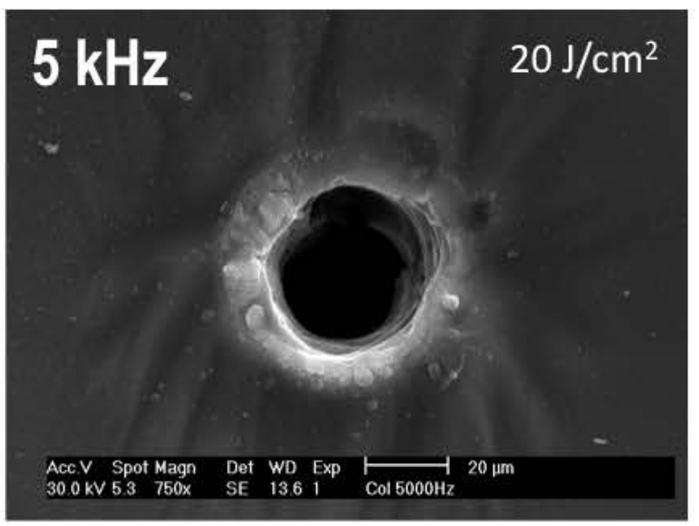








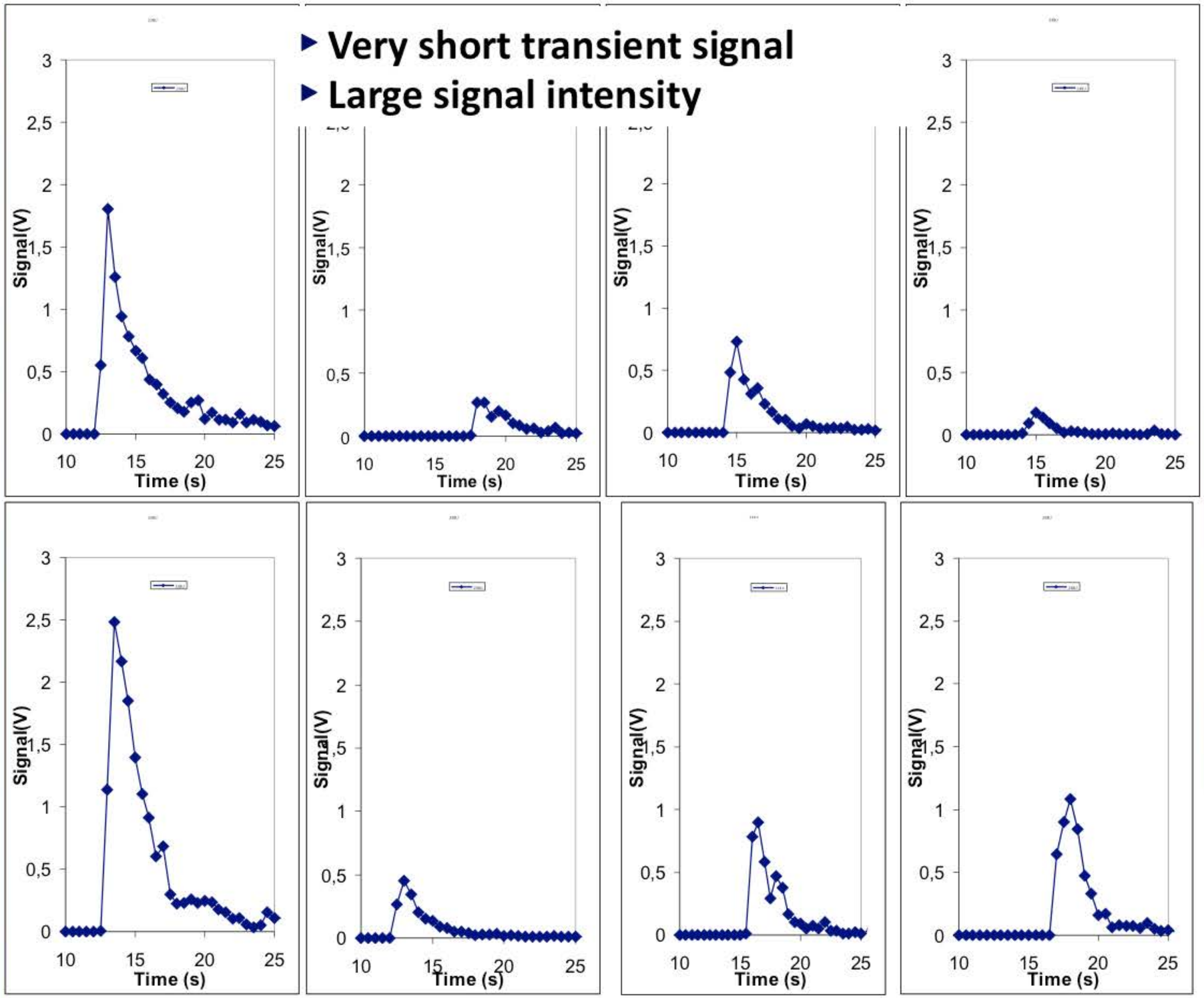




Uranium isotopic composition of micrometric particles

- Particles heterogeneity => size, shape, volume, density,…

- Very short transient signal
- Large signal intensity



- Particles of **Natural** Isotope composition

Ø 3 µm UO_2

238U: 150 pg

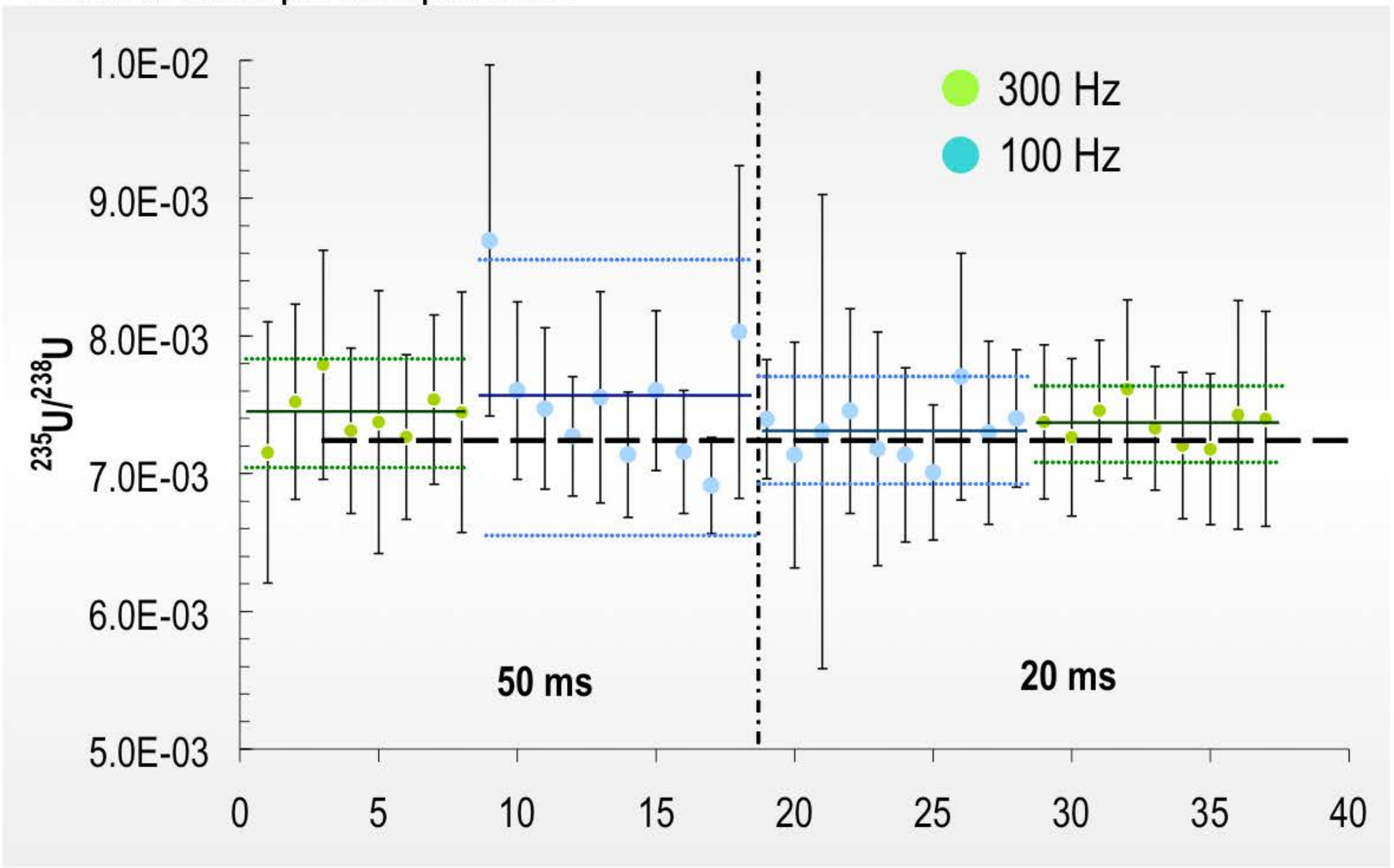
235U: 1 pg

234U: 8 fg

Uranium isotopic composition of micrometric particles

FsLA/ Quad ICPMS

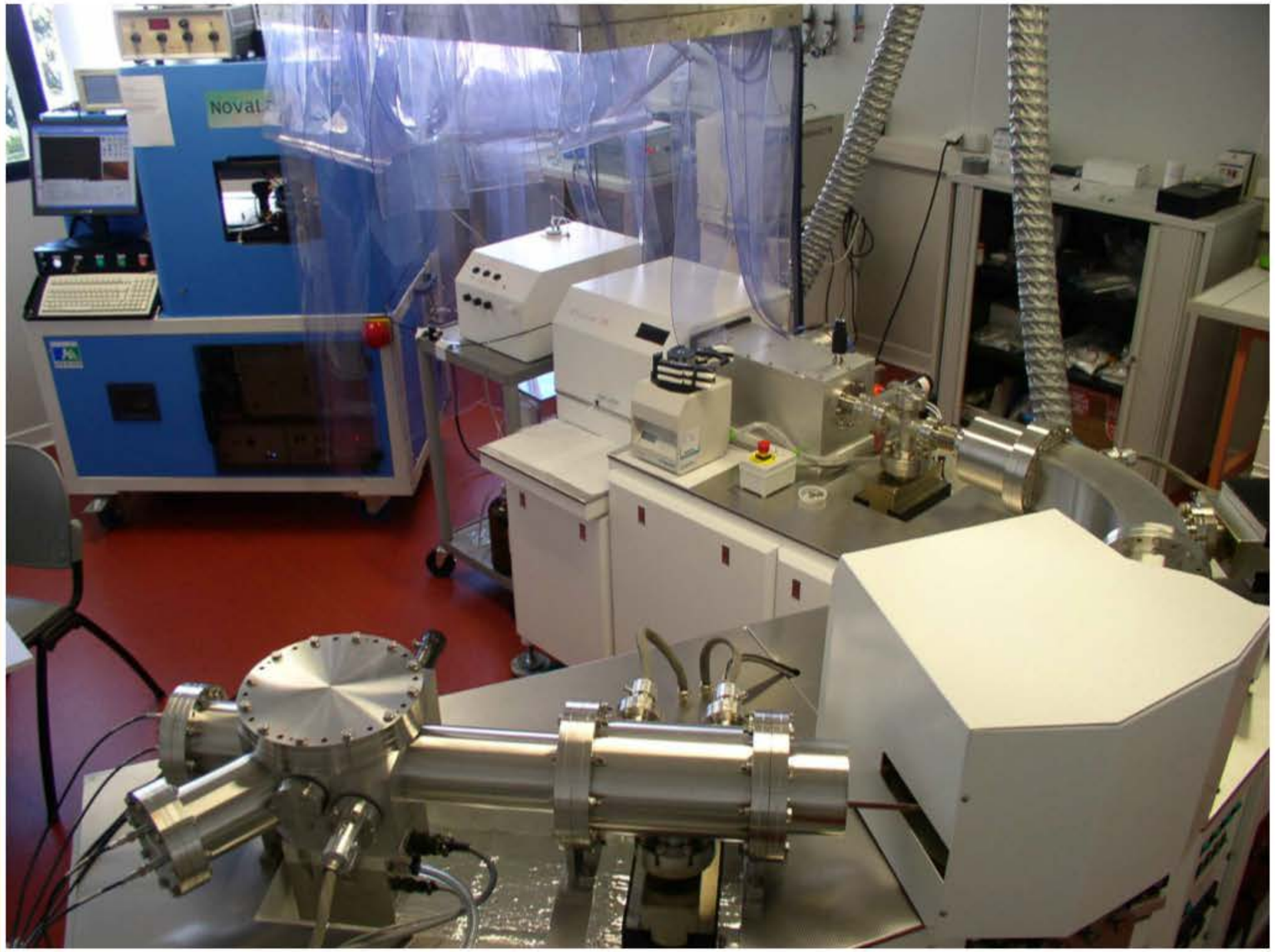
Natural Isotope composition



- Typical within run precision (1σ) = 7% to 15% for 235U/238U
- No reliable information on 234U nor 236U

Uranium isotopic composition of micrometric particles

- **Sector Field** => higher ion transmission,
  => higher sensitivity when using the IC



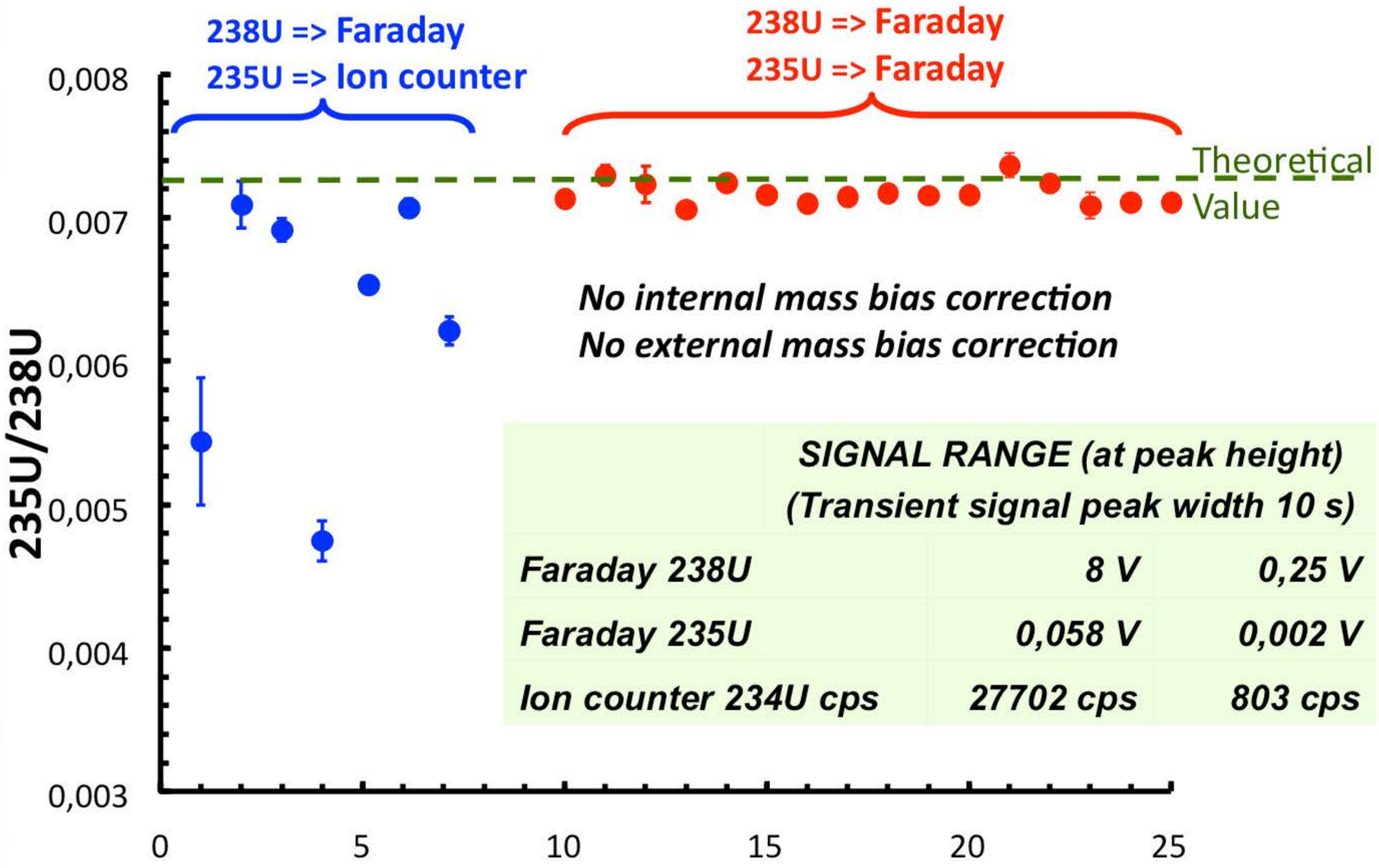
^{238}U, ^{235}U,

^{234}U, ^{236}U

MC-ICPMS -Nu Plasma HR

Uranium isotopic composition of micrometric particles

- **Effect of the detector…**



	SIGNAL RANGE (at peak height) (Transient signal peak width 10 s)	
Faraday 238U	*8 V*	*0,25 V*
Faraday 235U	*0,058 V*	*0,002 V*
Ion counter 234U cps	*27702 cps*	*803 cps*

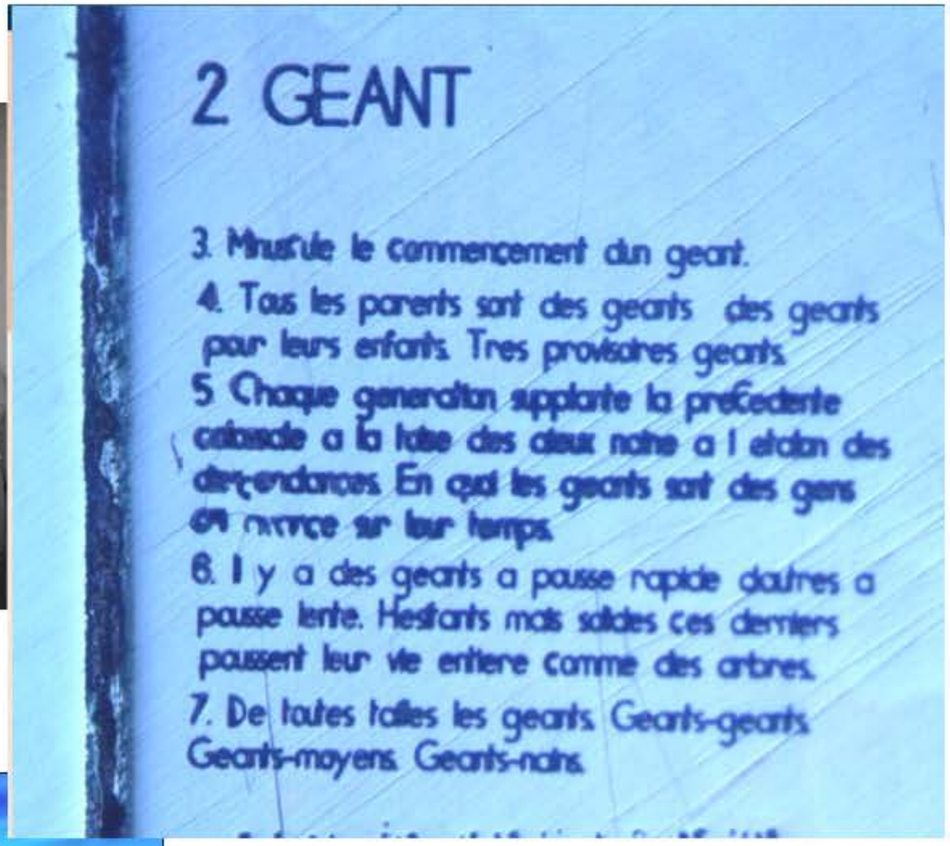
Uranium isotopic composition of micrometric particles

Comparing the analytical techniques…

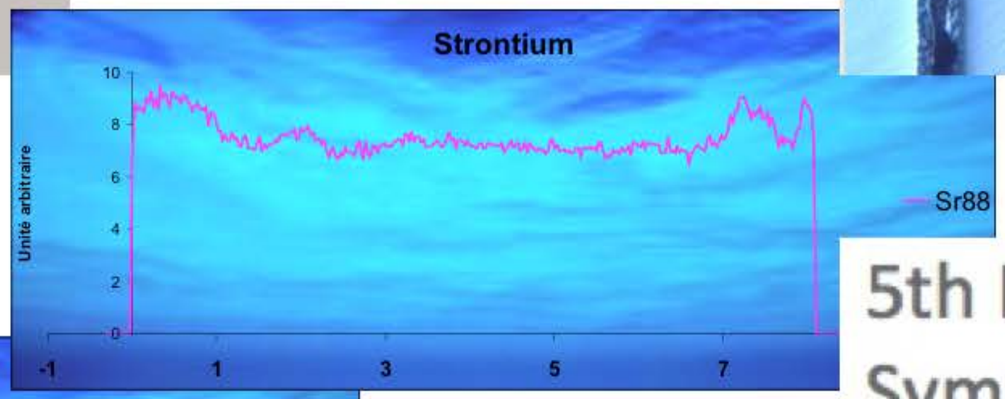
	235U/238U	234U/238U	
fsLA/Q-ICPMS			
Average Internal precision	10%	-	< 100 particles /day
Mean values (n=9)	0.00736 ±0,00027 (3,7%)	-	
Bias from theoretical value	1,5%	-	
fsLA/MC-ICPMS	*Faraday/Faraday*	*Ion counter/Faraday*	
Average Internal precision	0,68%	2.4%	< 100 particles /day
Mean values (n=16)	0.007178 ± 0.000084 (1,2%)	0.0000514 ± 0.0000014(3.2%)	
Bias from theoretical value	-1,04%	-7.2%	
FT-TIMS			
Average Internal precision	1.5%	-	< 6 particles /day
Mean values (n=5)	0.00740 ± 0.00004 (5.2%)	-	
Bias from theoretical value	2%	-	
SIMS			
Average Internal precision	0.2%	2%	< 24 particles /day
Mean values (n=6)	0.007246 ± 0.000058 (0.8%)	0.0000540 ± 0.0000011 (2%)	
Bias from theoretical value	-0.1%	-2.5%	

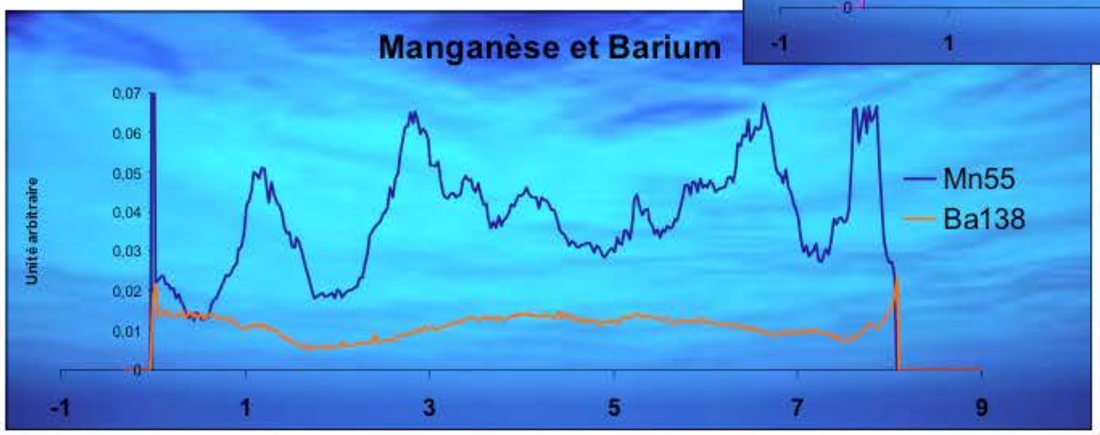
GEANT, PROTOLITHE

An artistic installation merging science and poetry....



Donatien Garnier
Christophe Pécheyran





5th International Otolith Symposium 2014 (IOS2014)

20-24 October 2014
Mallorca, Balearic Icelands
Spain