Consiglio Nazionale delle Ricerche
ISTITUTO DI GEOSCIENZE E GEORISORSE

PROGRAMMA NAZIONALE DI RICERCHE IN ANTARTIDE
ITALIANTARTIDE

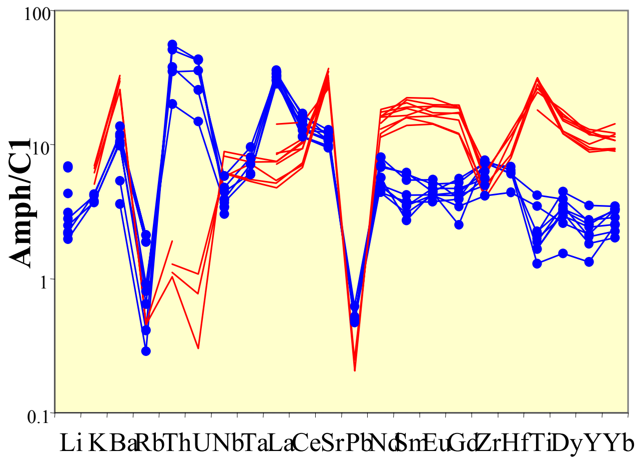
In-situ trace element and isotope determinations with laser ablation (LA)-HR-ICPMS & (LA)-MC-ICPMS

M. Tiepolo
C.N.R.-Istituto di Geoscienze e Georisorse Sezione di Pavia, Italy

Thanks to:
C. Bouman, B. Narcisi, F. Schiavi, M. Palenzona, J-L. Paquette, M.R. Renna, R. Tribuzio, R. Vannucci, A. Zanetti

Geochemistry of the solid Earth

Trace elements



Radiogenic & Stable isotopes

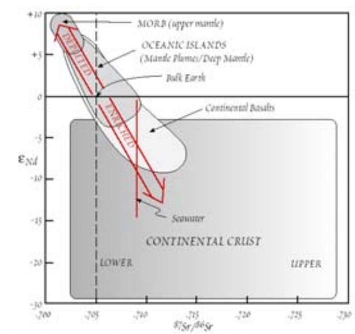
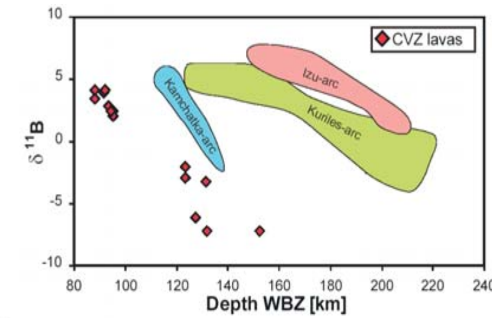
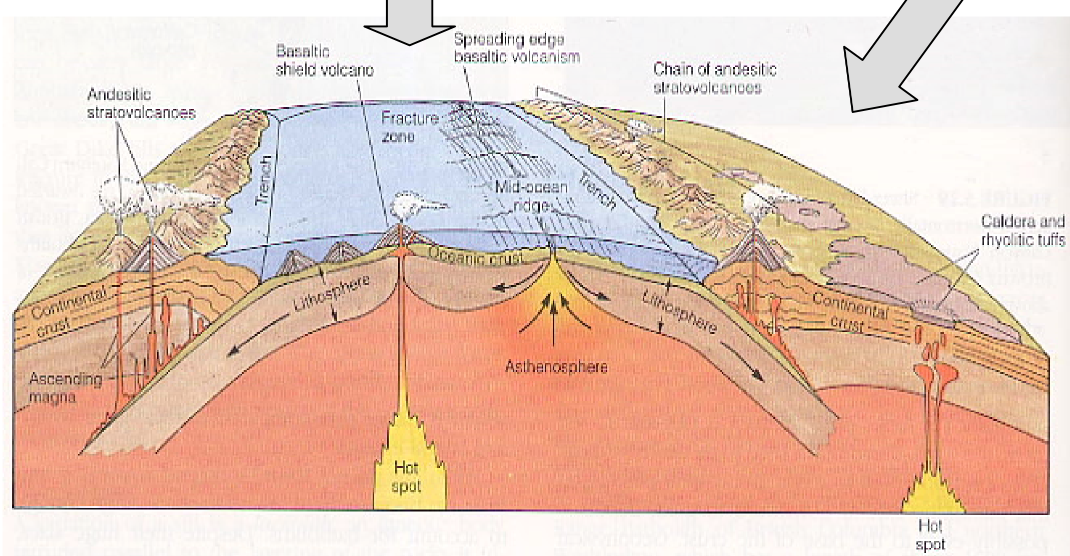
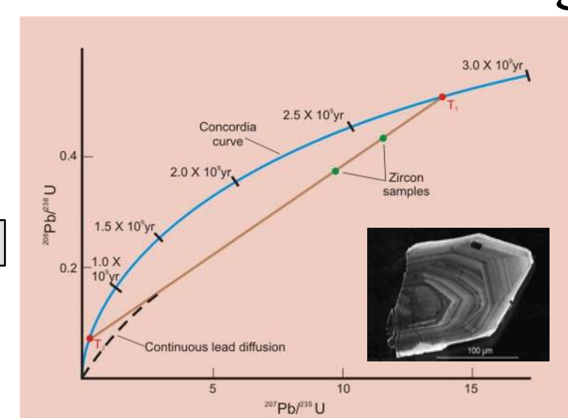


Figure 8.11. Sr and Nd isotope ratios in major geochemical reservoirs. The isotopic composition of the bulk Earth lies at the intersection of the horizontal line at ε_{Nd} = 0 and the dashed vertical line at $^{87}Sr/^{86}Sr$ = 0.705 (the latter is dashed because the bulk Earth $^{87}Sr/^{86}Sr$ is somewhat uncertain). Arrows labeled 'enriched' and 'depleted' show where incompatible element enriched and depleted reservoirs would plot.





Geochronology

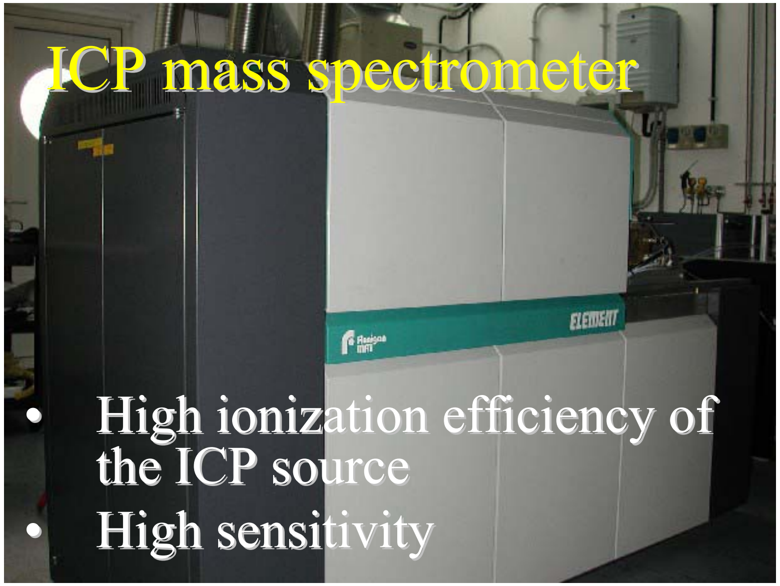


Approximate scale of precision

Trace element	5-10%
Geochronology (U-Pb)	1-2%
Isotope geochemistry	<< 1%

Laser ablation (LA)-ICP-MS

+

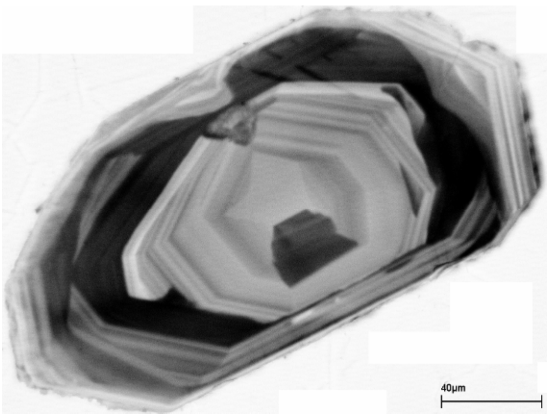


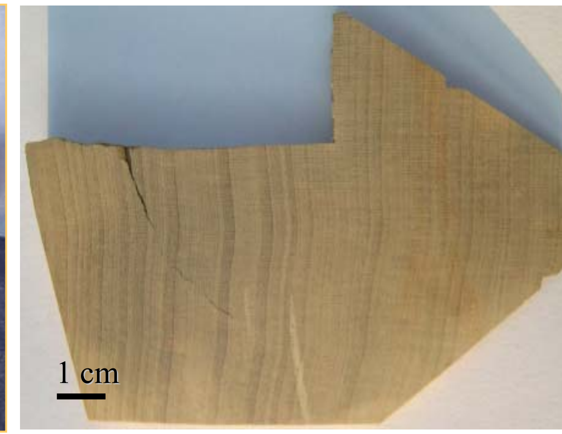
Trace element and isotopic determinations

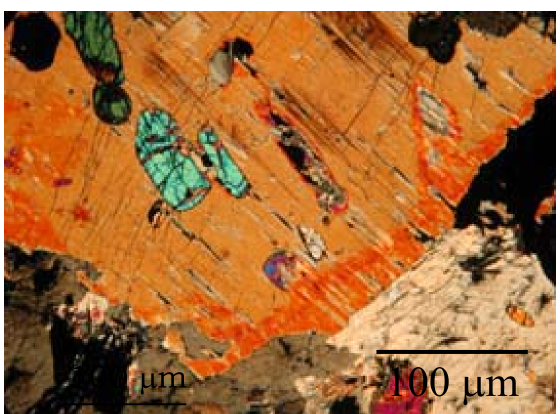
↓

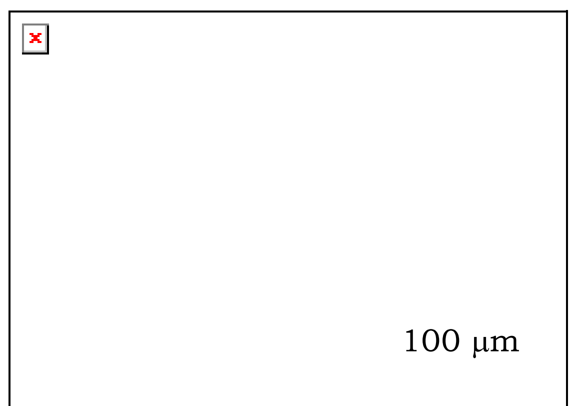
Earth Sciences, environmental sciences, biological sciences, forensic sciences, semiconductors

Examples of materials where the *in situ* approach is required









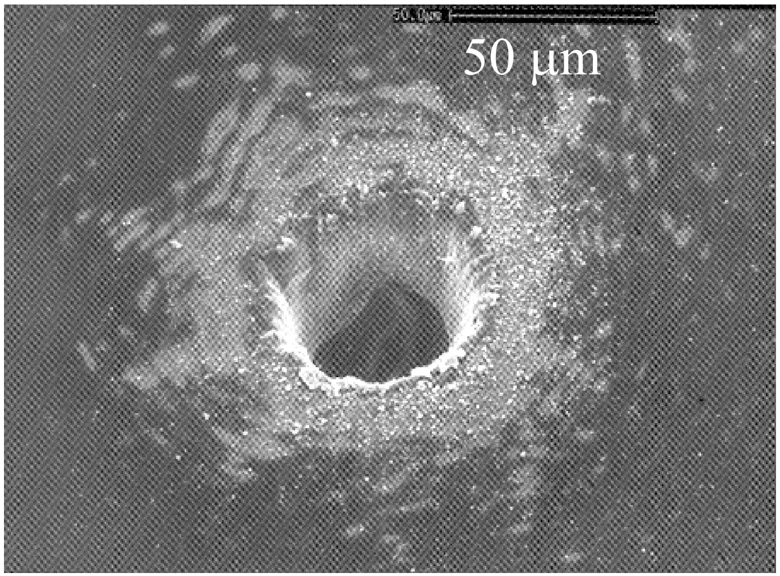
Rocks & Minerals

Volcanic ashes

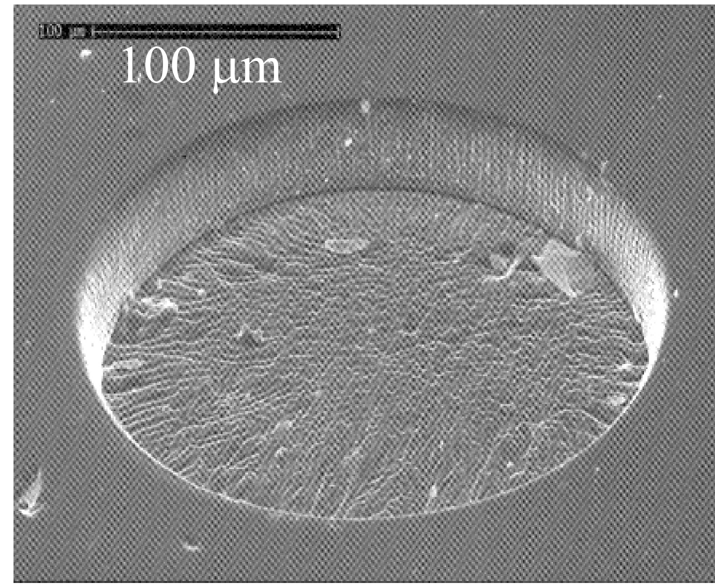
Tree ring analyses

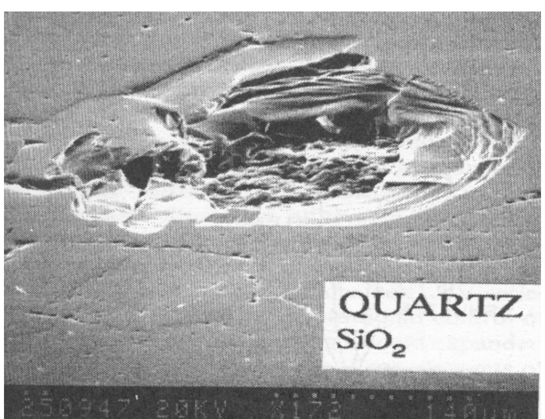
Laser wavelengths and laser pits

266 nm Nd:YAG laser



193 nm ArF Excimer laser



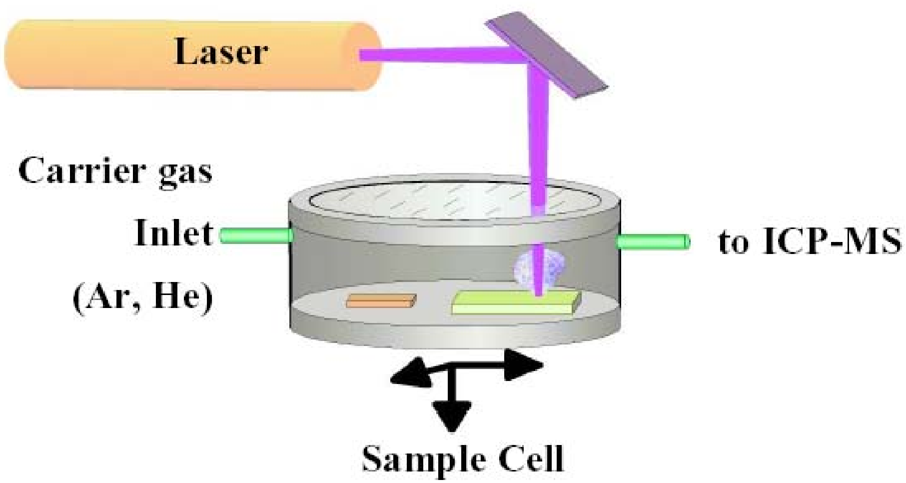


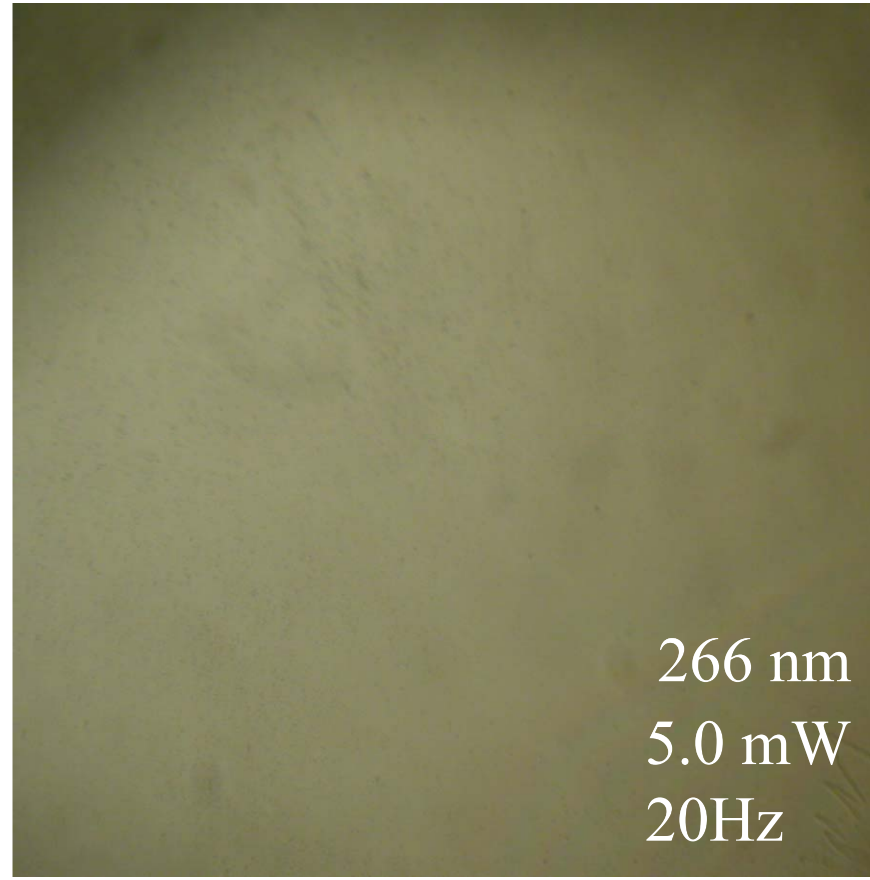
Ablation efficiency is a function of:

- Laser wavelength ($E_{193} > E_{266}$)
- Material (UV transparency)

The ablation process

BCR-2
Basaltic glass





100 µm

Sensitivity in laser ablation (Dry plasma)

Signal from laser ablation is about **100,000** times lower than that from solution nebulisation.

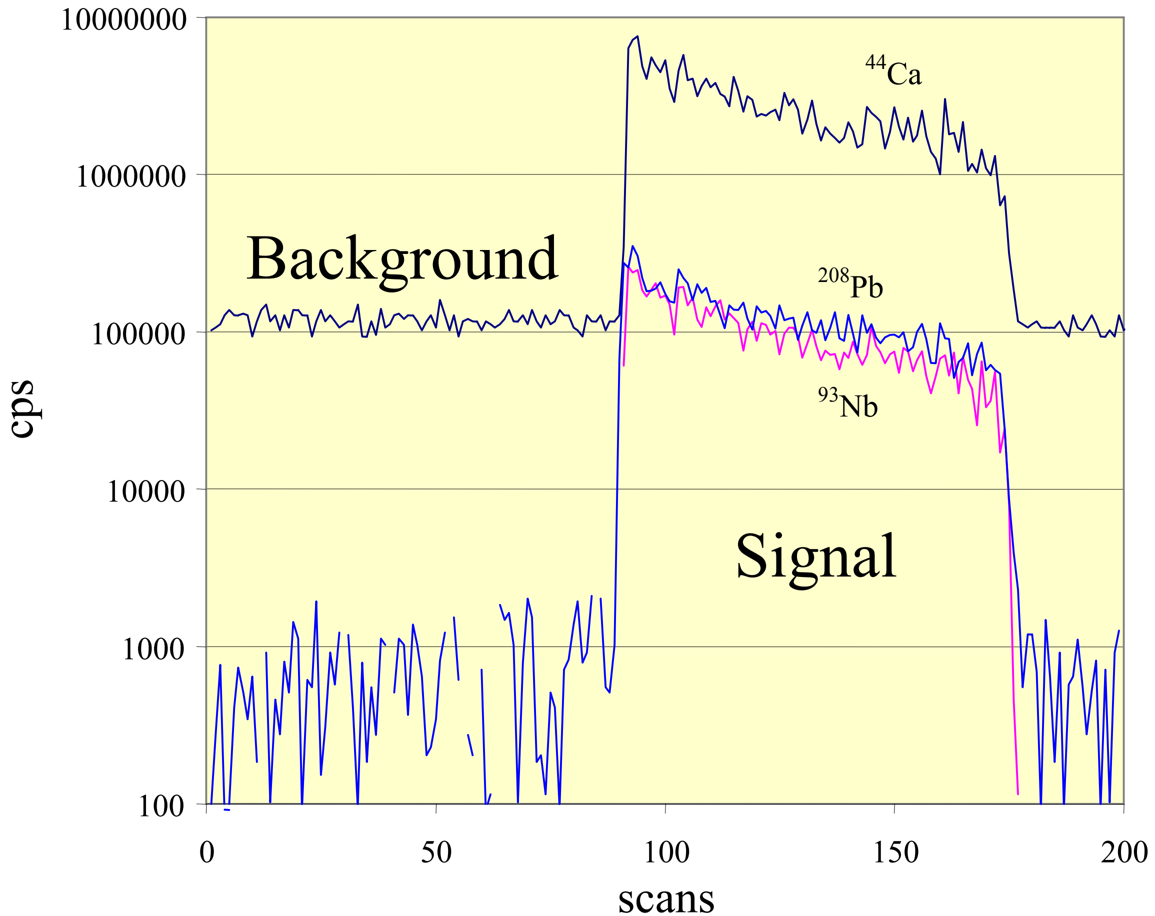
example

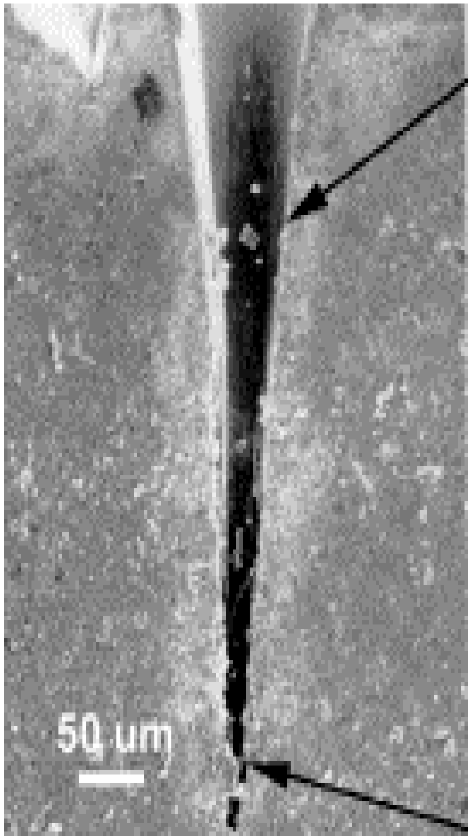
$1x10^9$ cps/ppm In → **$1x10^4$** cps/ppm In

This enormous difference is mainly related to the poor efficiency of the ICP torch in ionising the particulate produced by laser ablation.

The laser ablation signal

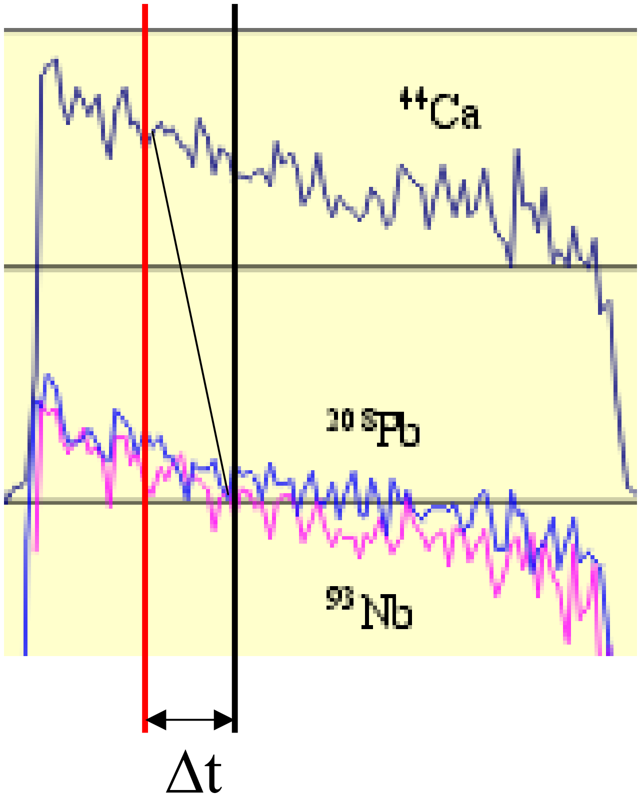
1. <u>Highly transient</u> (signal decrease with time/depth)
2. <u>Limited in time</u> (~ 2 minutes of signal)



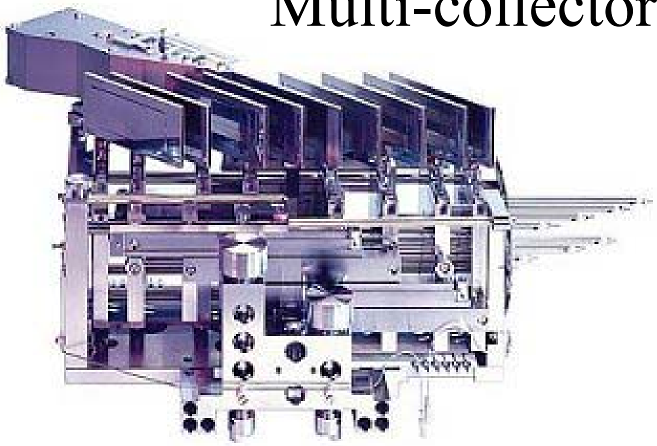


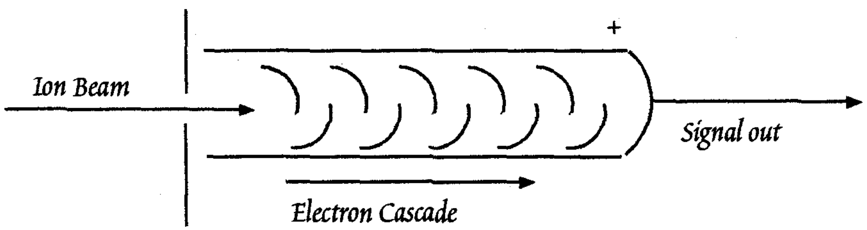
Signal acquisition

Simultaneous vs. Sequential



Multi-collector





Single collector

$$({}^{44}Ca/{}^{208}Pb)_m = f\,[\Delta t\,;\,({}^{44}Ca/{}^{208}Pb)_S]$$

Requirements of the ICPMS

- *High sensitivity* (high signal/background ratio)

- *Multi–element analysis*

  → High scan speed

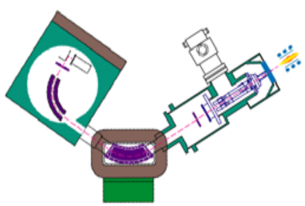
- *Isotope analysis*

  → High abundance sensitivity
  Flat top peaks
  (Possibly) multi collectors

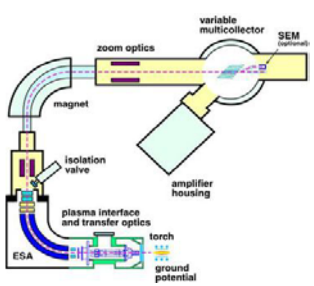
ICPMS and applications

- **<u>Q-ICP-MS</u>** → highest scan speed
  - Multi-element analysis

- **<u>HR-ICPMS</u>** → high sensitivity – relatively high scan speed – flat top peaks
  - Multi element analysis (depleted samples)
  - Basic isotope analysis (Pb geochronology)

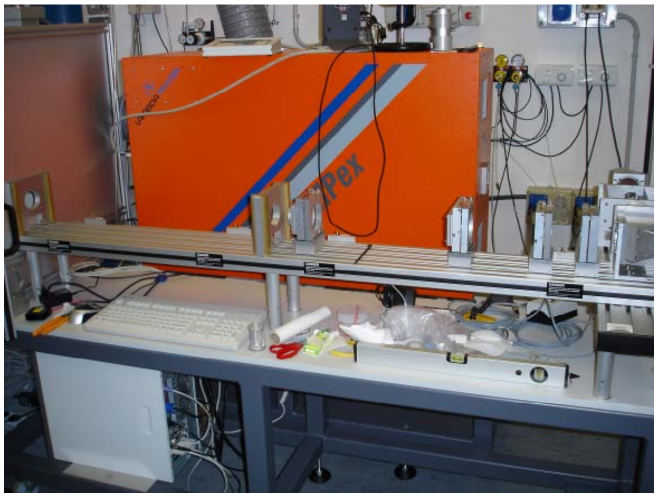


- **<u>MC-ICP-MS</u>** → high sensitivity - multi collector – no dynamic scan
  - Advanced isotope analysis
  - *<u>No multi element analysis</u>*

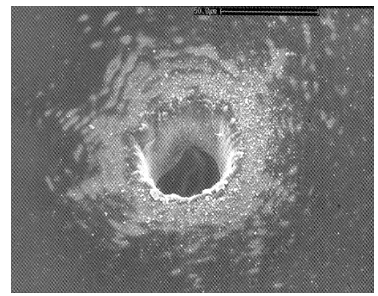


SINGLE COLLECTOR HIGH RESOLUTION (HR)-ICPMS

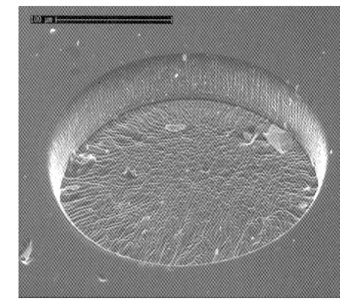
Multi element analyses with LA-HR-ICPMS



Nd:Yag 266 nm



ArF Excimer 193 nm



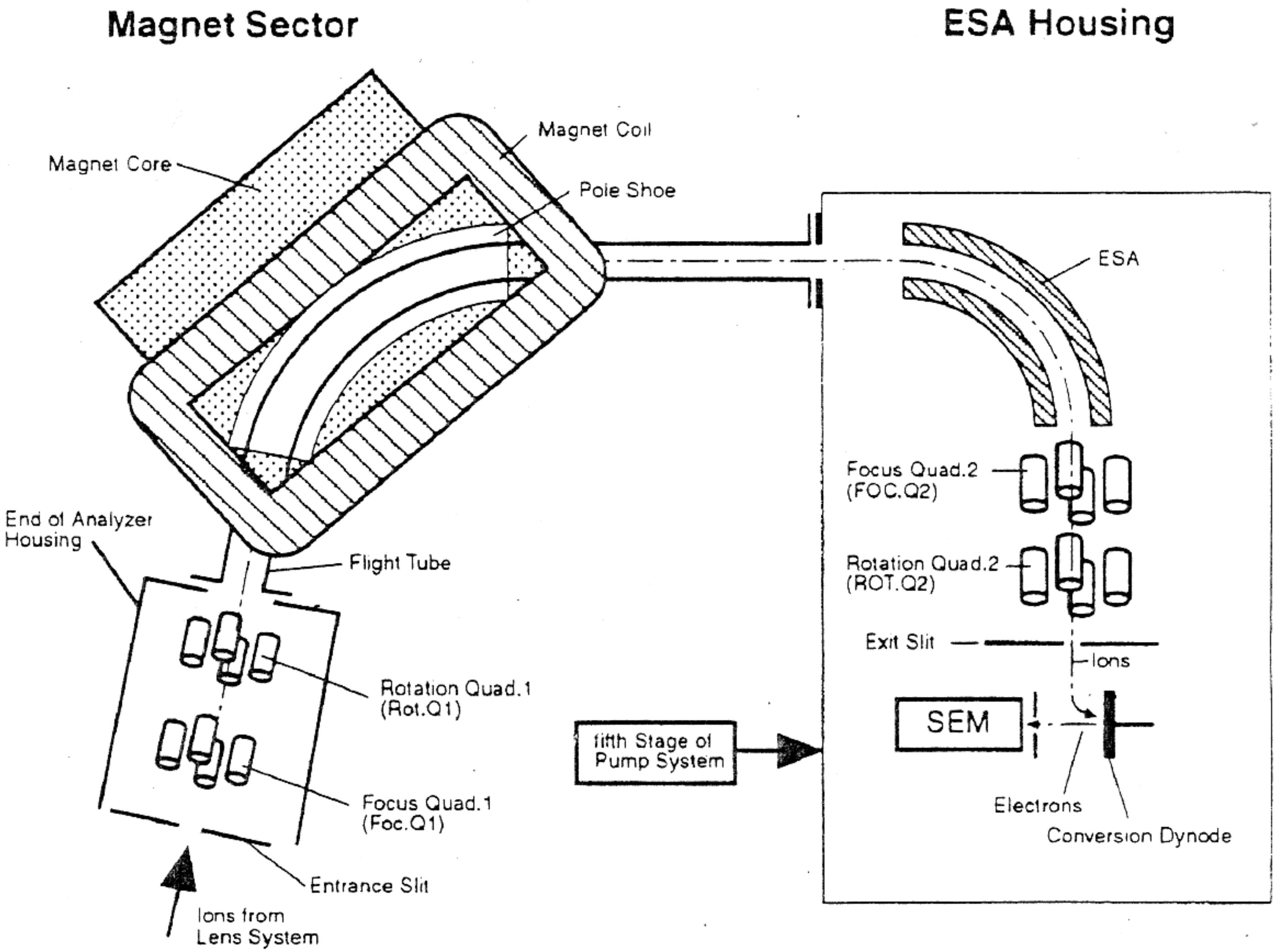
Element I

(ThermoFinnigan)

Upgraded to Element II for:

- Capacitive decoupling torch
- Magnet
- Magnet field regulator

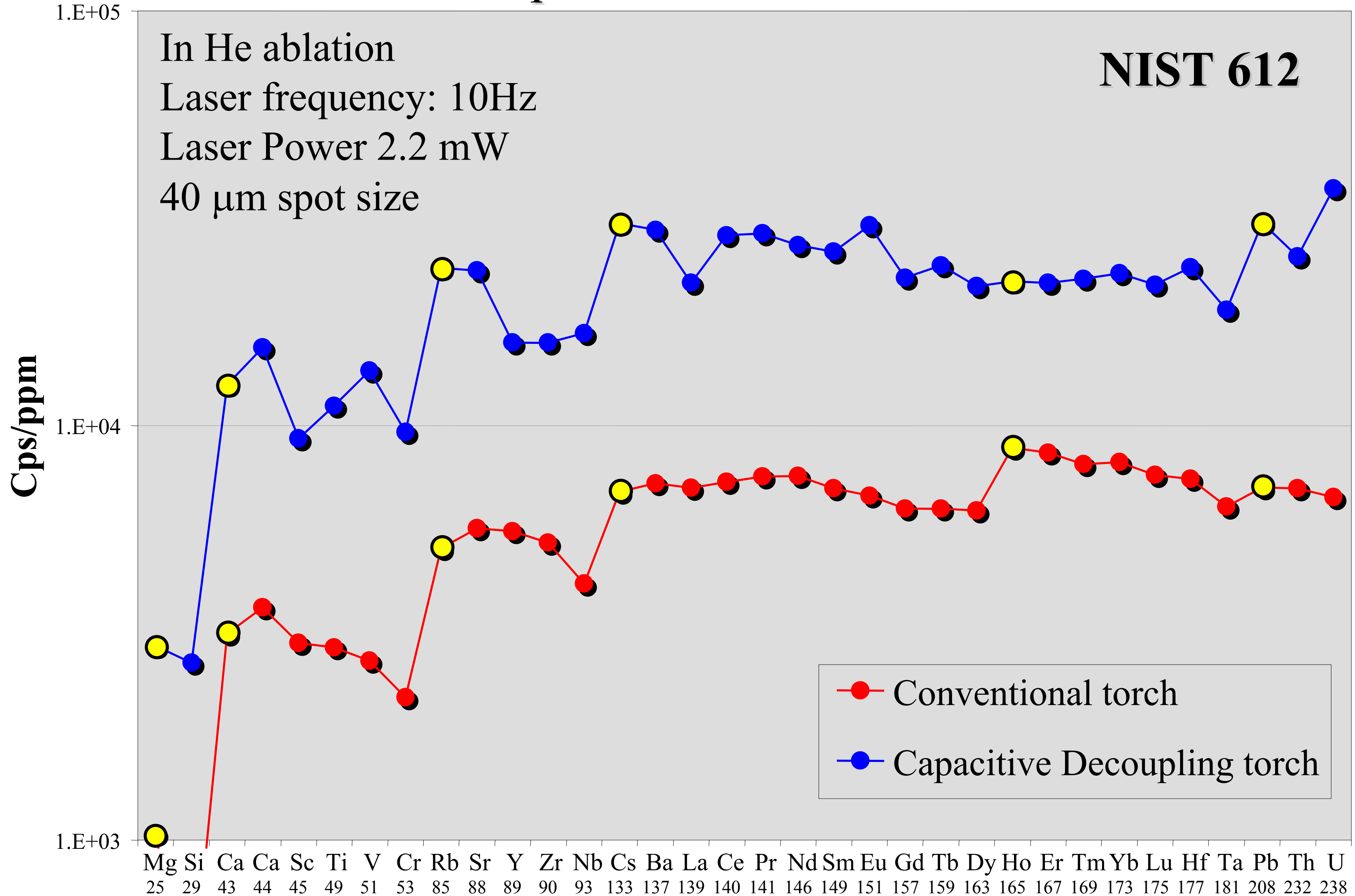
Layout of the HR-ICPMS



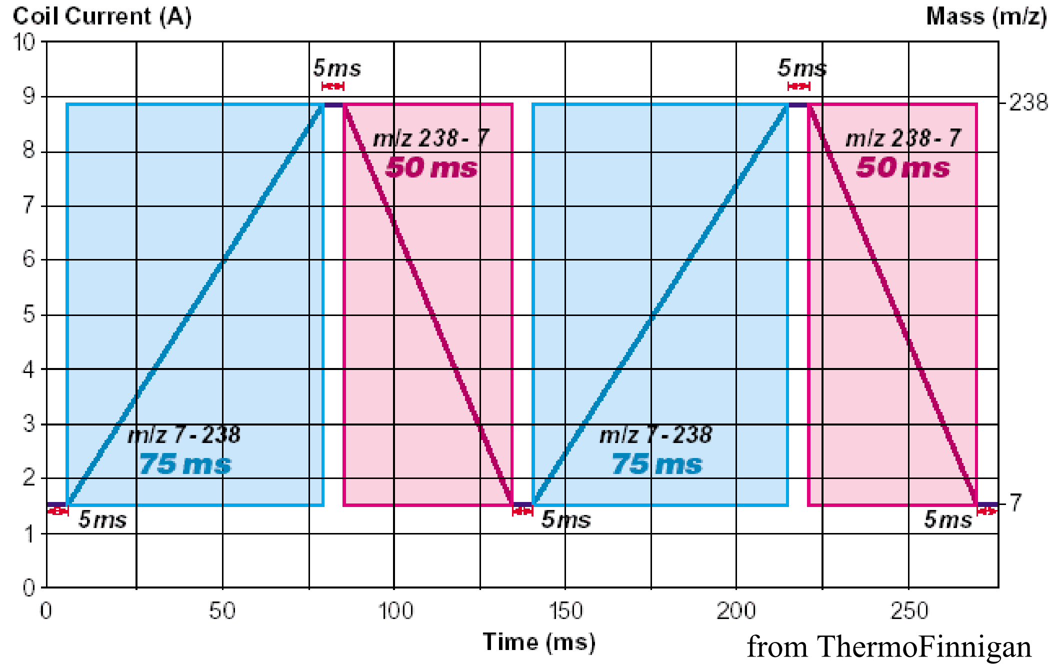
from ThermoFinnigan

Response curve

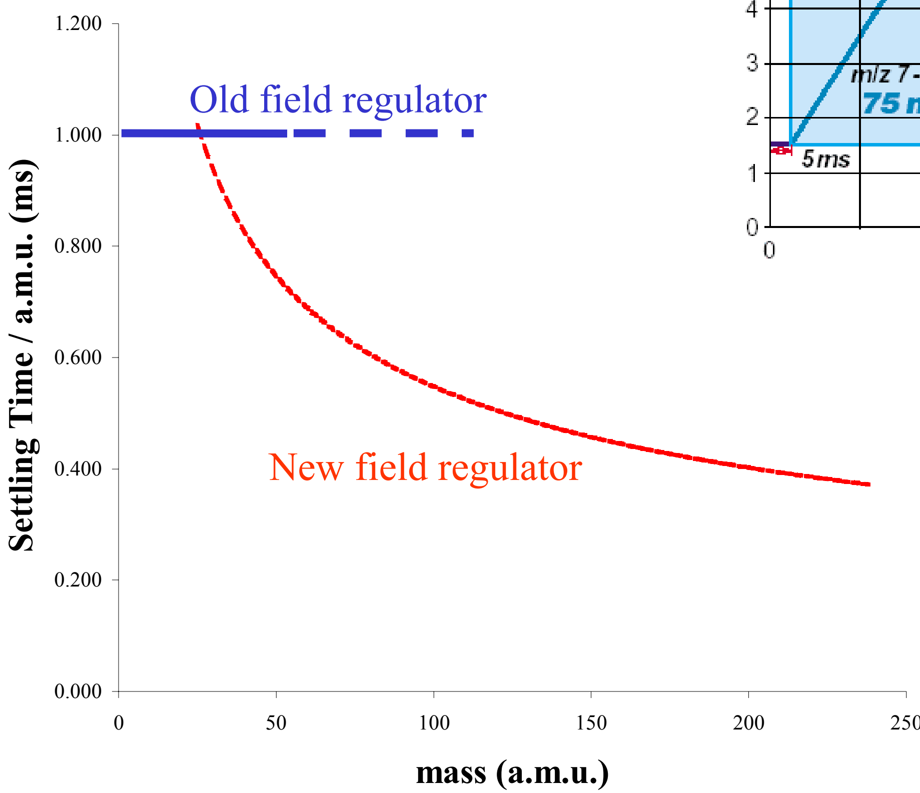
Isotopic abundance normalized



"High power magnet field regulator"



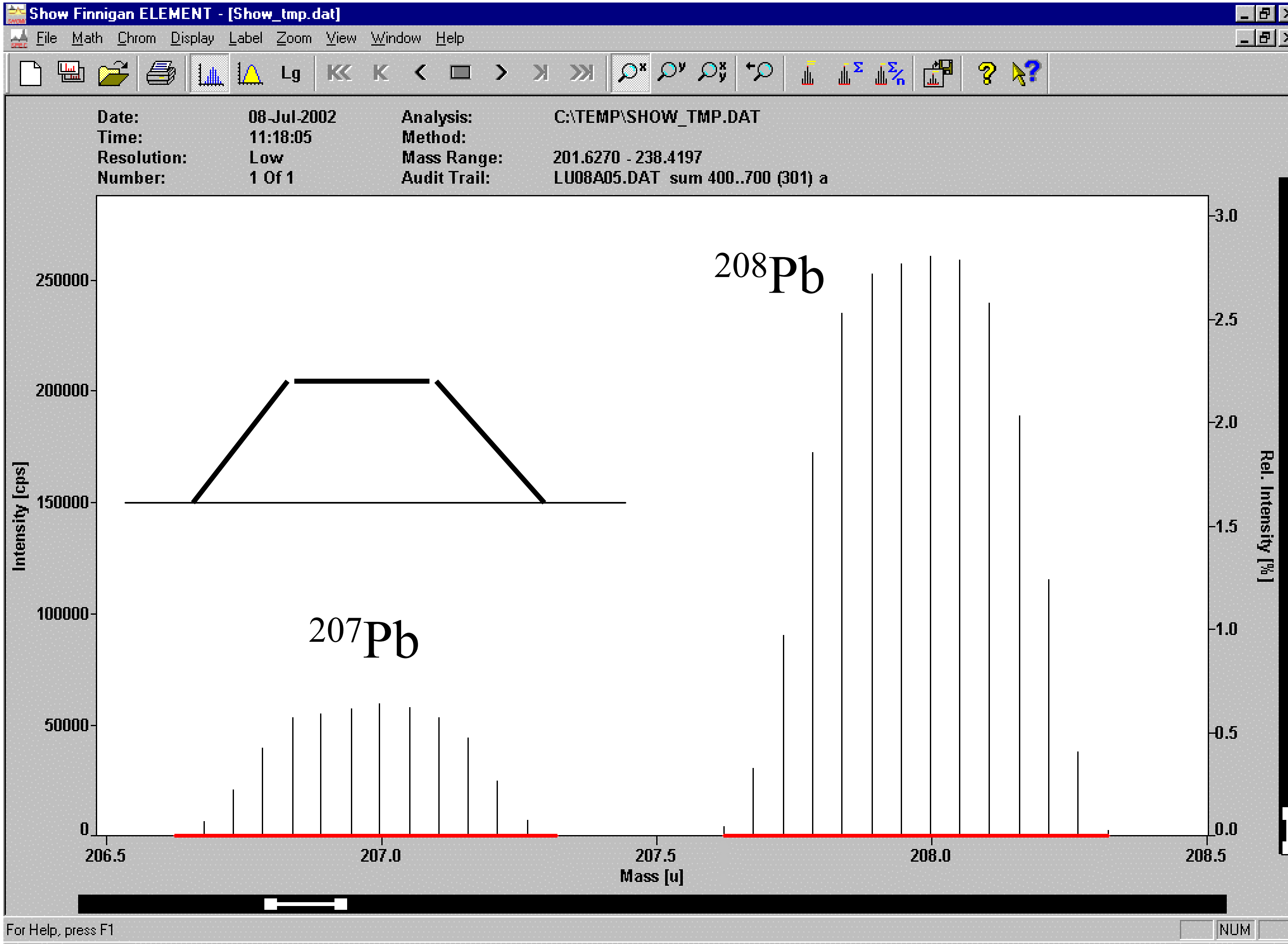
from ThermoFinnigan



m/z 7-238 **230 ms**

m/z 7-238 **75 ms**

“Flat top” peaks



Multi element determinations (Low Res.)

$^{7}Li \rightarrow {}^{238}U$ (36 masses)

*Scan time: **624 ms***

B-scan

E-scan

^{6}Li

^{7}Li

^{25}Mg

^{29}Si

^{43}Ca $\rightarrow {}^{44}Ca \rightarrow {}^{45}Sc \rightarrow {}^{49}Ti$

^{51}V $\rightarrow {}^{53}Cr \rightarrow {}^{59}Co$

^{85}Rb $\rightarrow {}^{88}Sr \rightarrow {}^{89}Y \rightarrow {}^{90}Zr \rightarrow {}^{93}Nb$

^{133}Cs $\rightarrow {}^{137}Ba \rightarrow {}^{139}La \rightarrow {}^{140}Ce \rightarrow {}^{141}Pr \rightarrow {}^{146}Nd \rightarrow {}^{149}Sm \rightarrow {}^{151}Eu$

^{157}Gd $\rightarrow {}^{159}Tb \rightarrow {}^{163}Dy \rightarrow {}^{165}Ho \rightarrow {}^{167}Er \rightarrow {}^{169}Tm \rightarrow {}^{173}Yb \rightarrow {}^{175}Lu \rightarrow {}^{177}Hf \rightarrow {}^{181}Ta$

^{208}Pb $\rightarrow {}^{232}Th \rightarrow {}^{238}U$

$^{6}Li \rightarrow {}^{44}Ca$

isotope
^{6}Li
^{7}Li
^{9}Be
^{11}B
^{25}Mg
^{29}Si
^{44}Ca

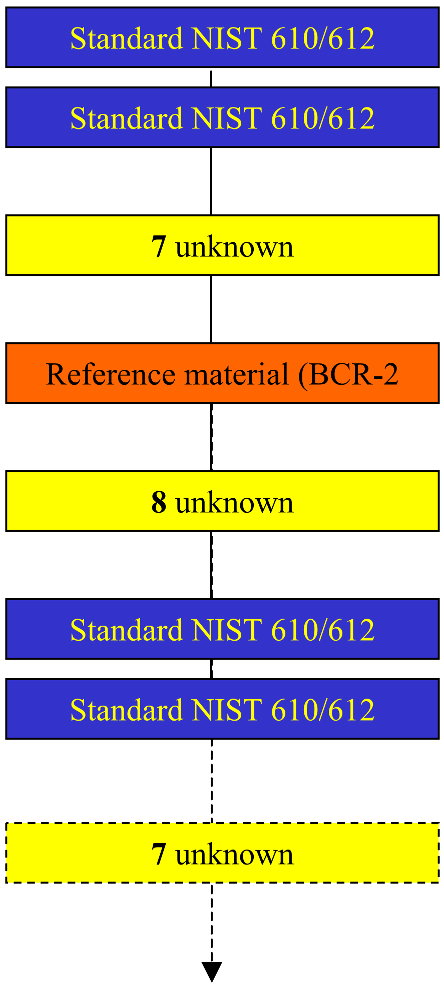
Total scan time: 196 ms

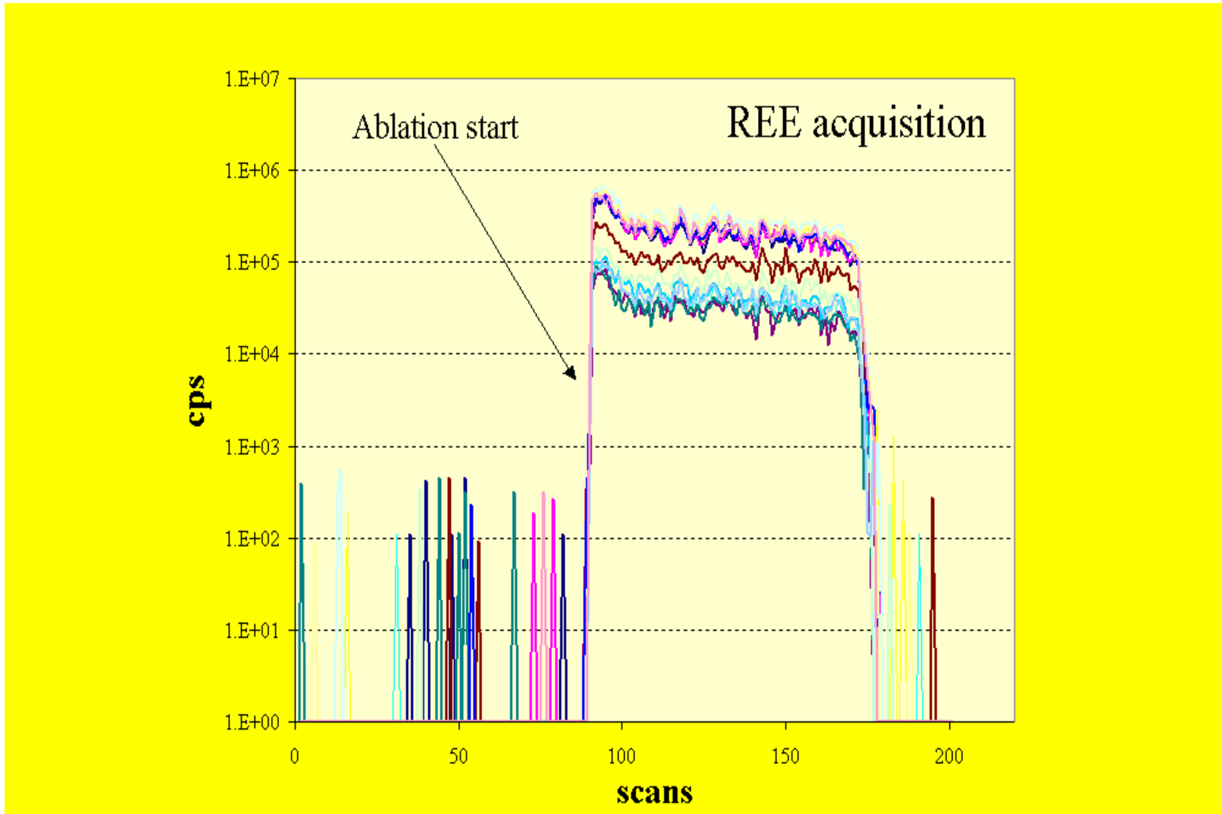
Acquisition efficiency: 60%

All masses are almost free from interferences and XO^+/X^+ ratio < 1%

Data acquisition

1 minute Background – 1 minute Signal



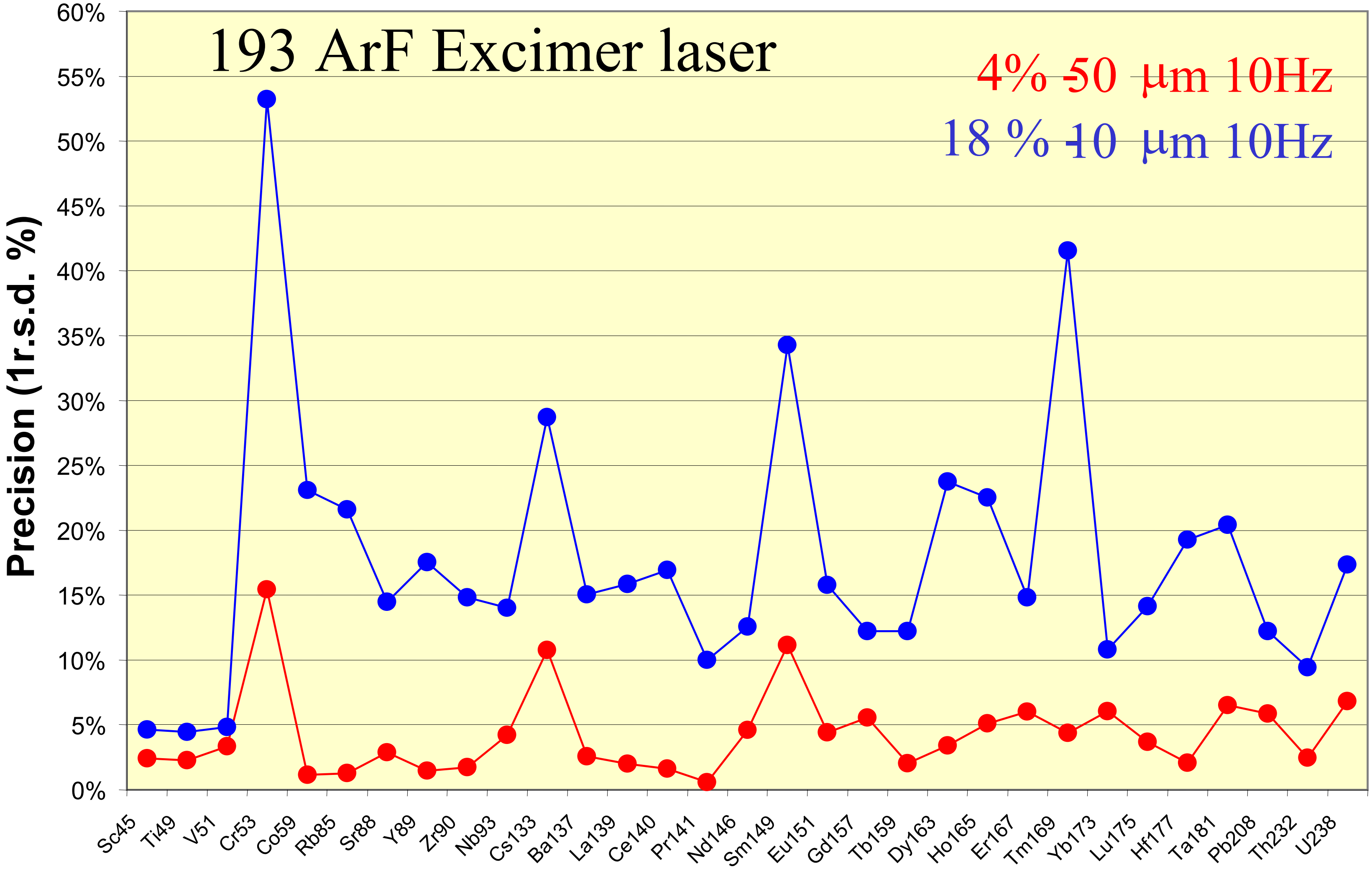


$$C_i^{SAMP} = \frac{C_i^{STD} \cdot I_i^{SAMP}}{I_i^{STD} \cdot RSF}$$

$$RSF = \frac{C_{is}^{STD} \cdot I_{is}^{SAMP}}{I_{is}^{STD} C_{is}^{SAMP}}$$

Precision

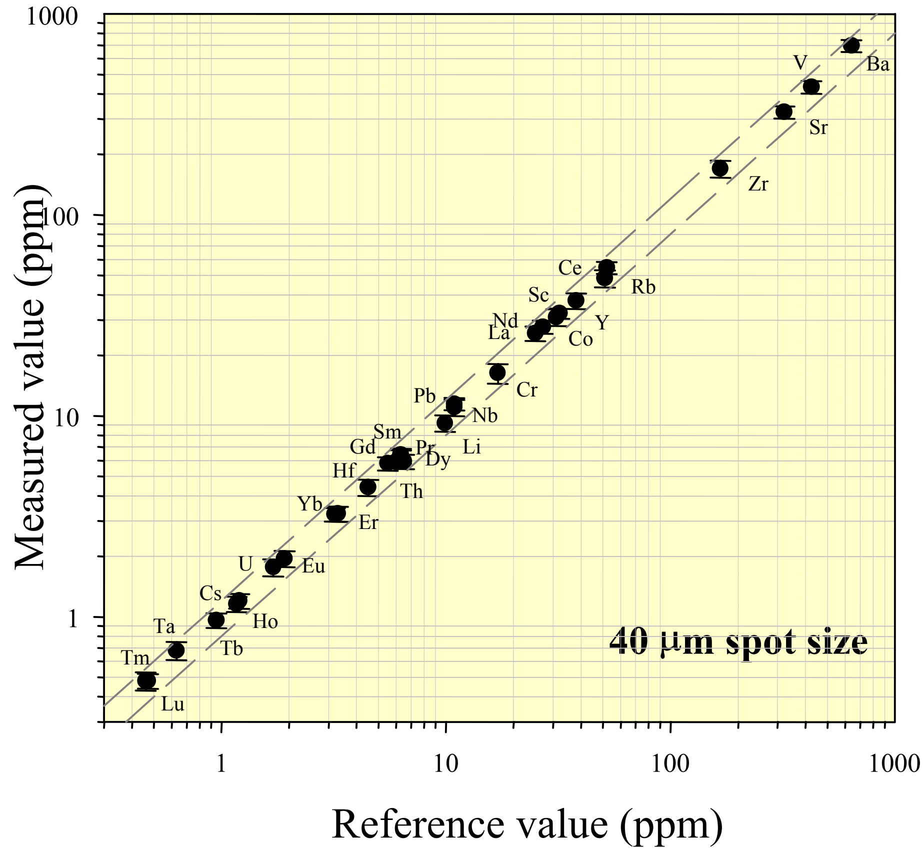
USGS - BCR-2 (basalt glass)

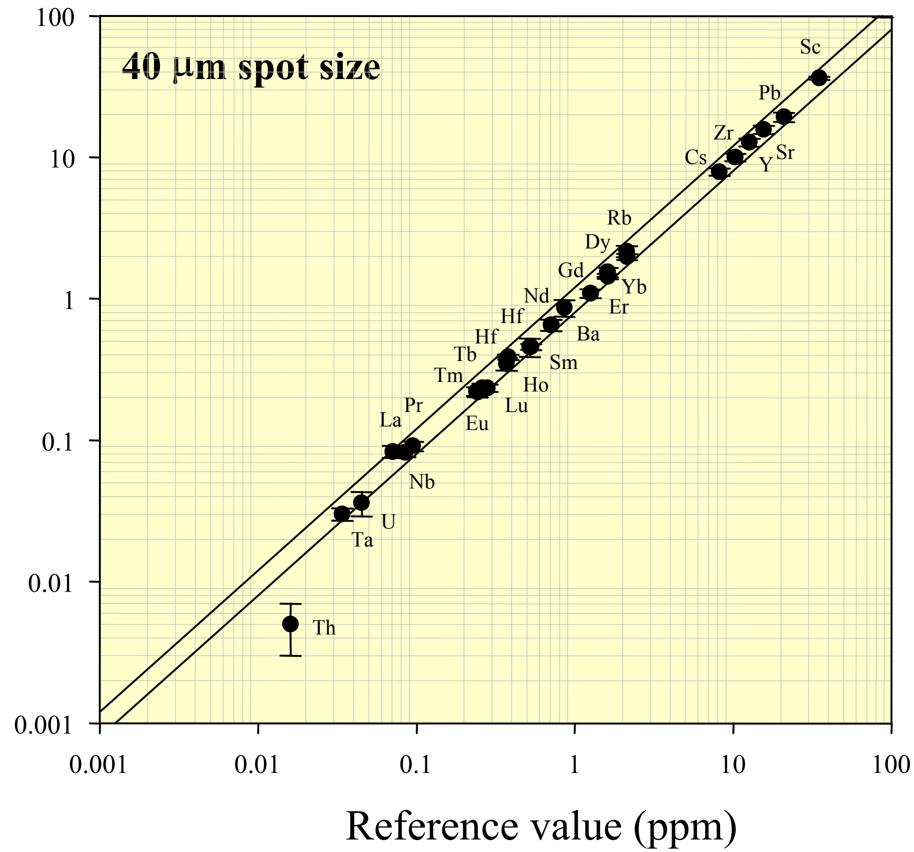


Accuracy

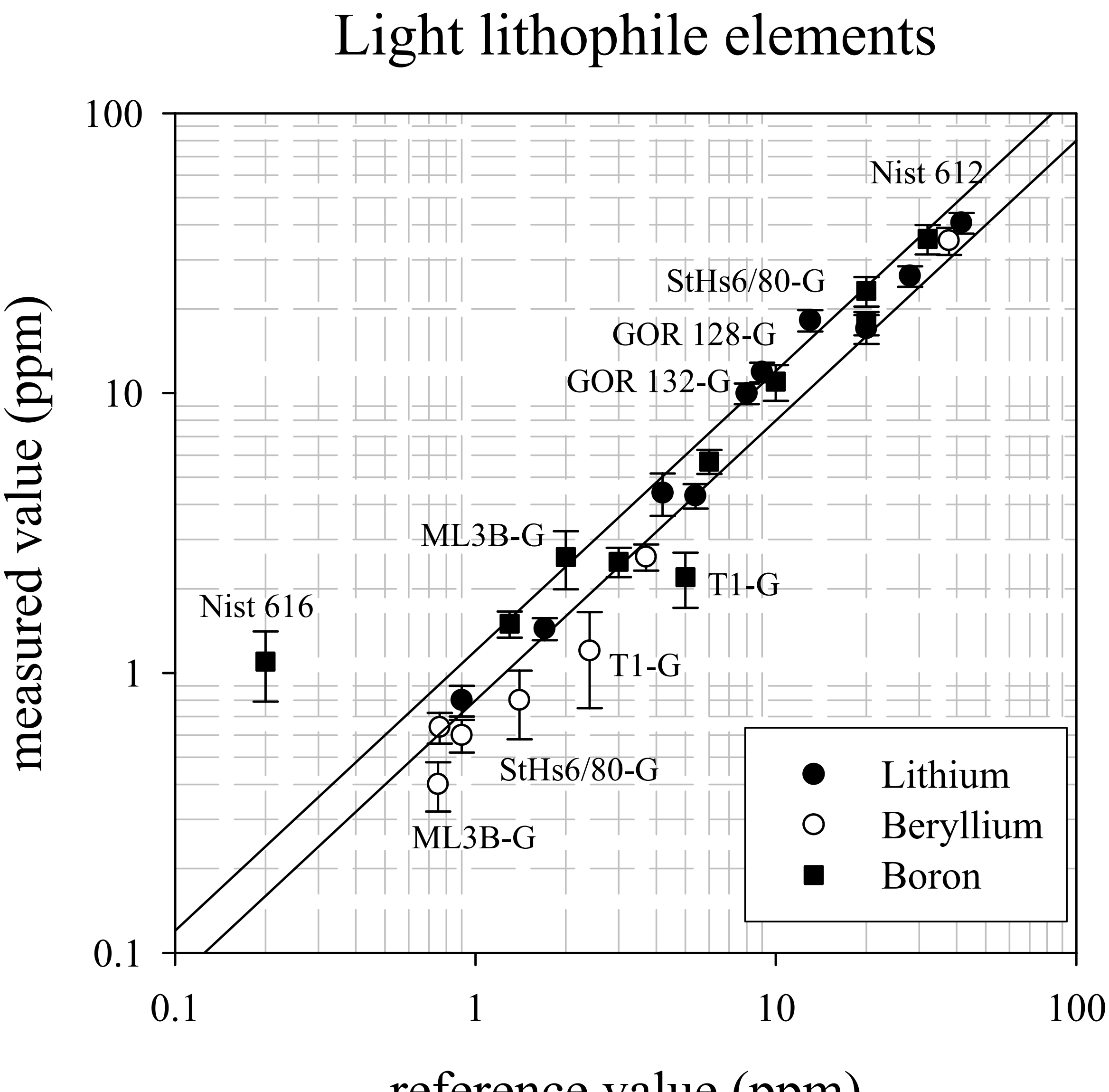
(extended trace elements)

USGS - BCR-2 (basalt glass)   MPI-DING GOR 128-G



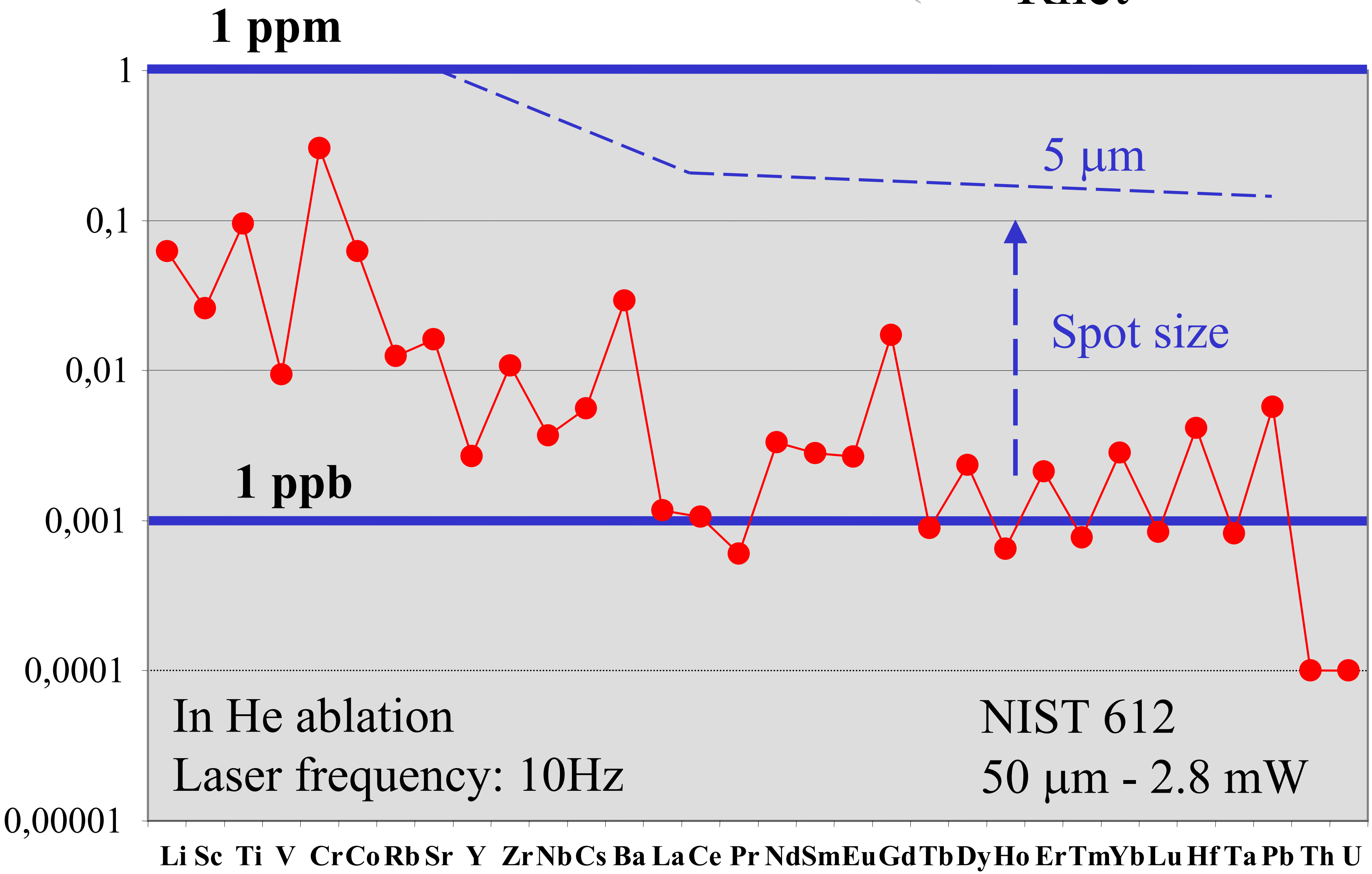


Accuracy

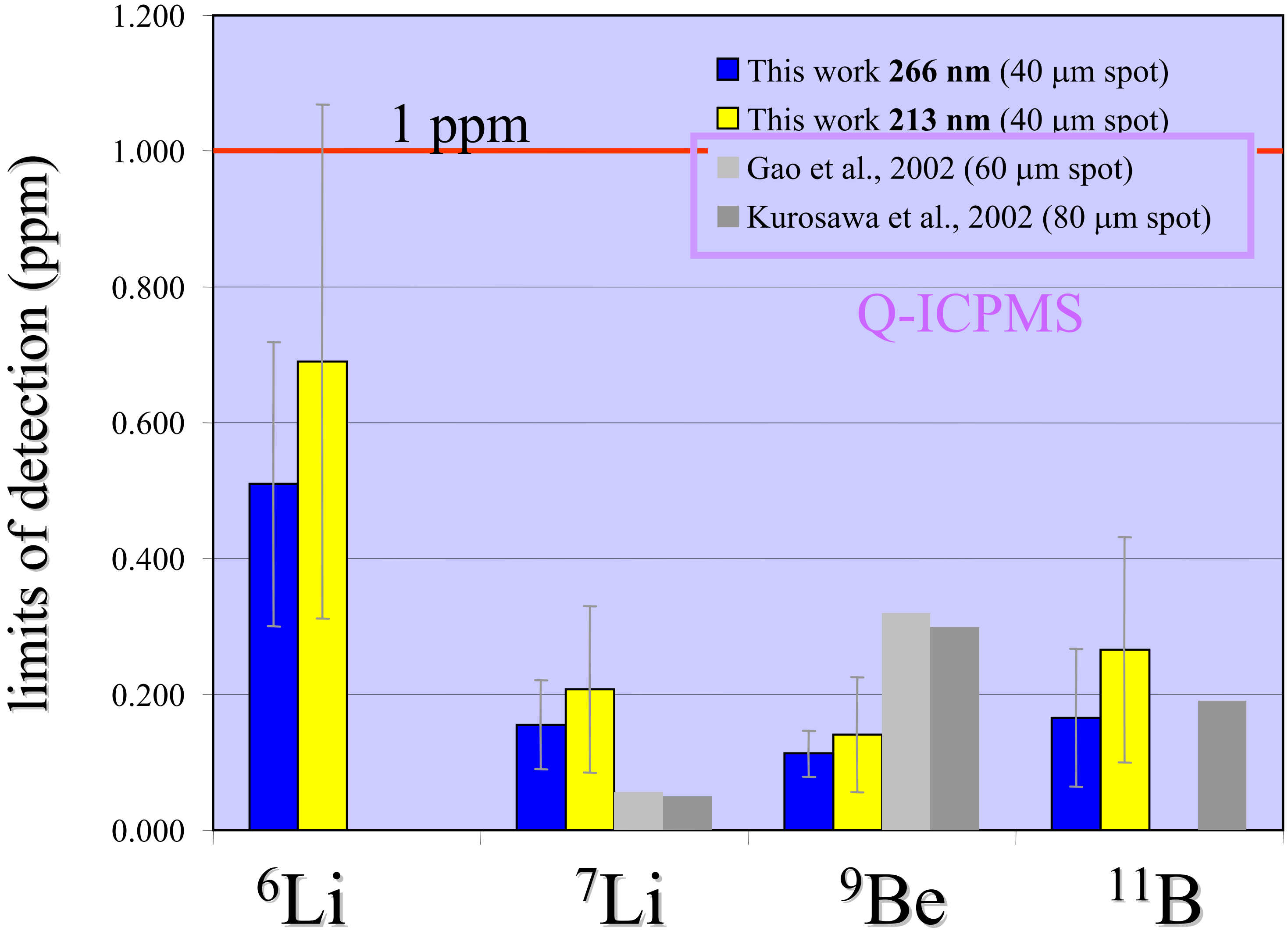


Light lithophile elements
100
10
1
0.1
0.1
1
10
100
measured value (ppm)
reference value (ppm)
Nist 612
StHs6/80-G
GOR 128-G
GOR 132-G
ML3B-G
T1-G
Nist 616
T1-G
StHs6/80-G
ML3B-G
Lithium
Beryllium
Boron

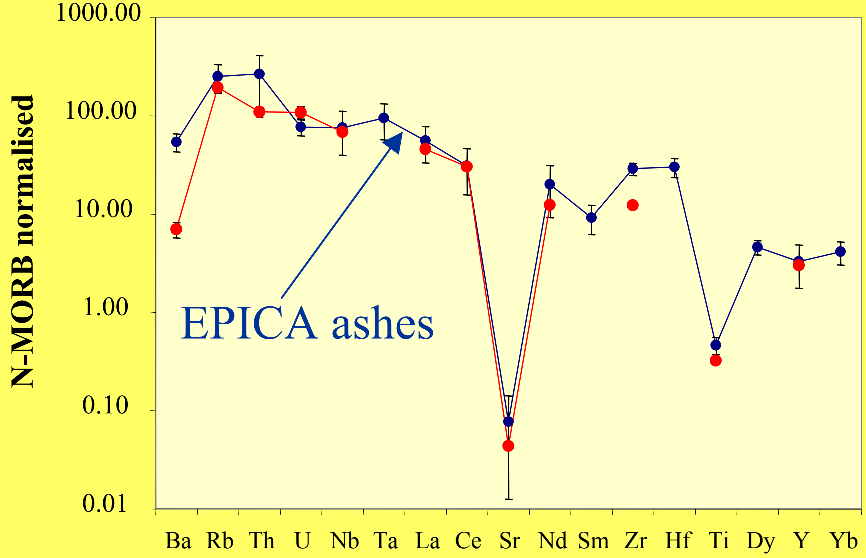
Limits of detection ($3\sigma_{Rnet}/S$)



Limits of detection (LLE)

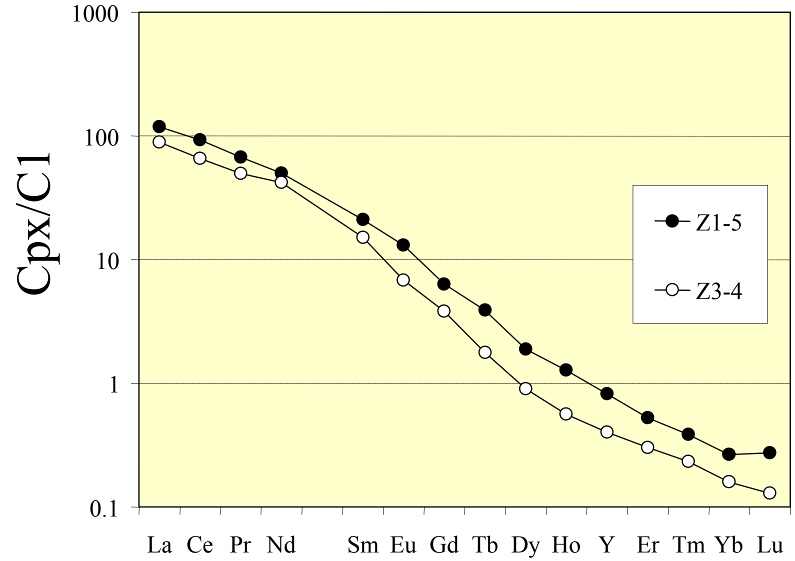


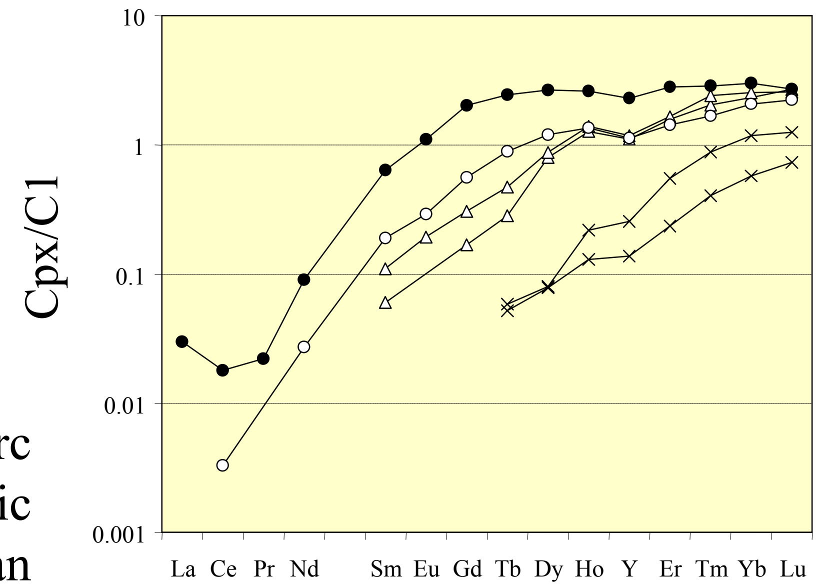
APPLICATIONS:
1) Geological samples



Volcanic ash in Ice cores from Antarctica (5µm – 193 nm)

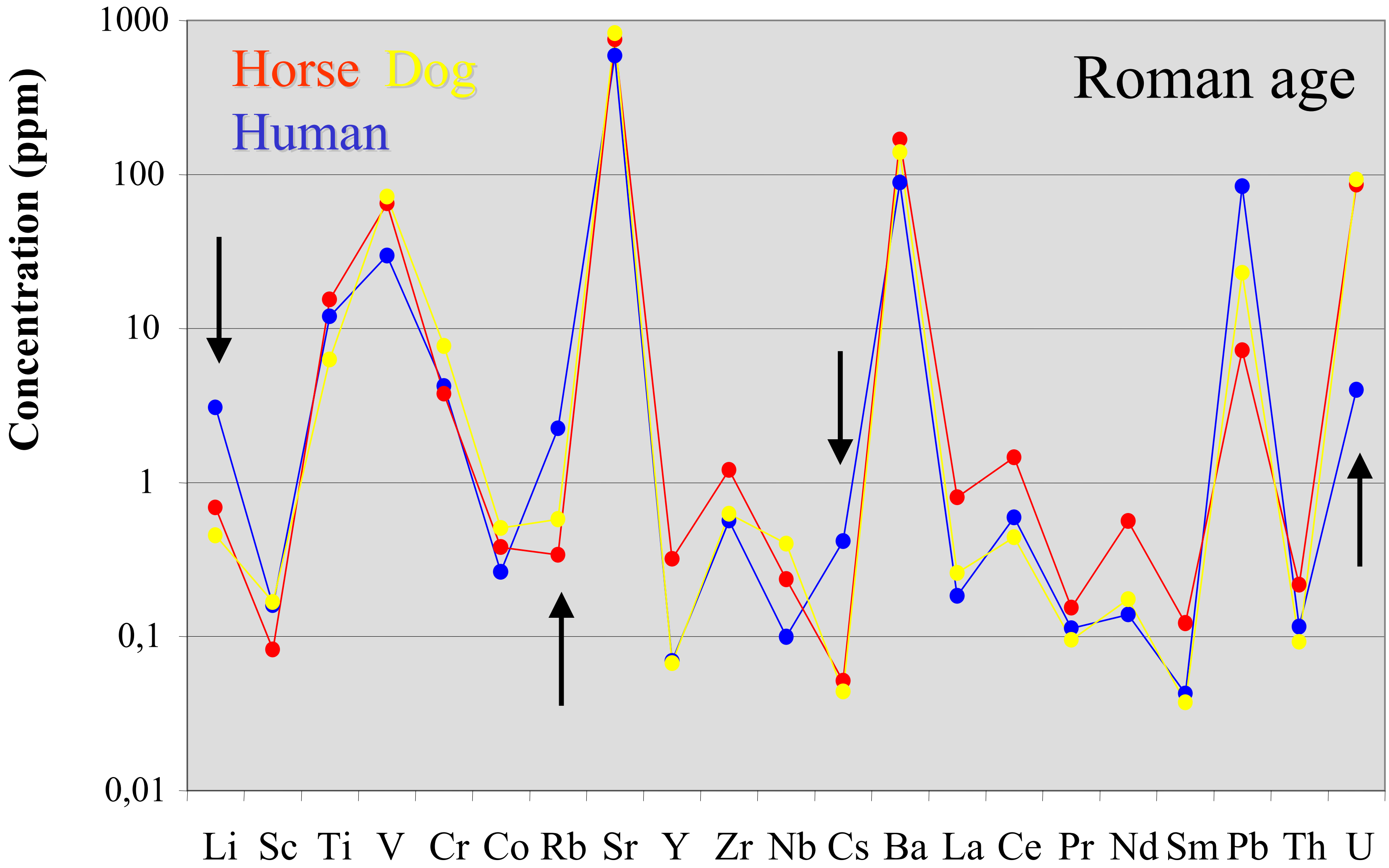
Clinopyroxene from Zagadochnaya kimberlite (Siberian craton of Yakutia, Russia)



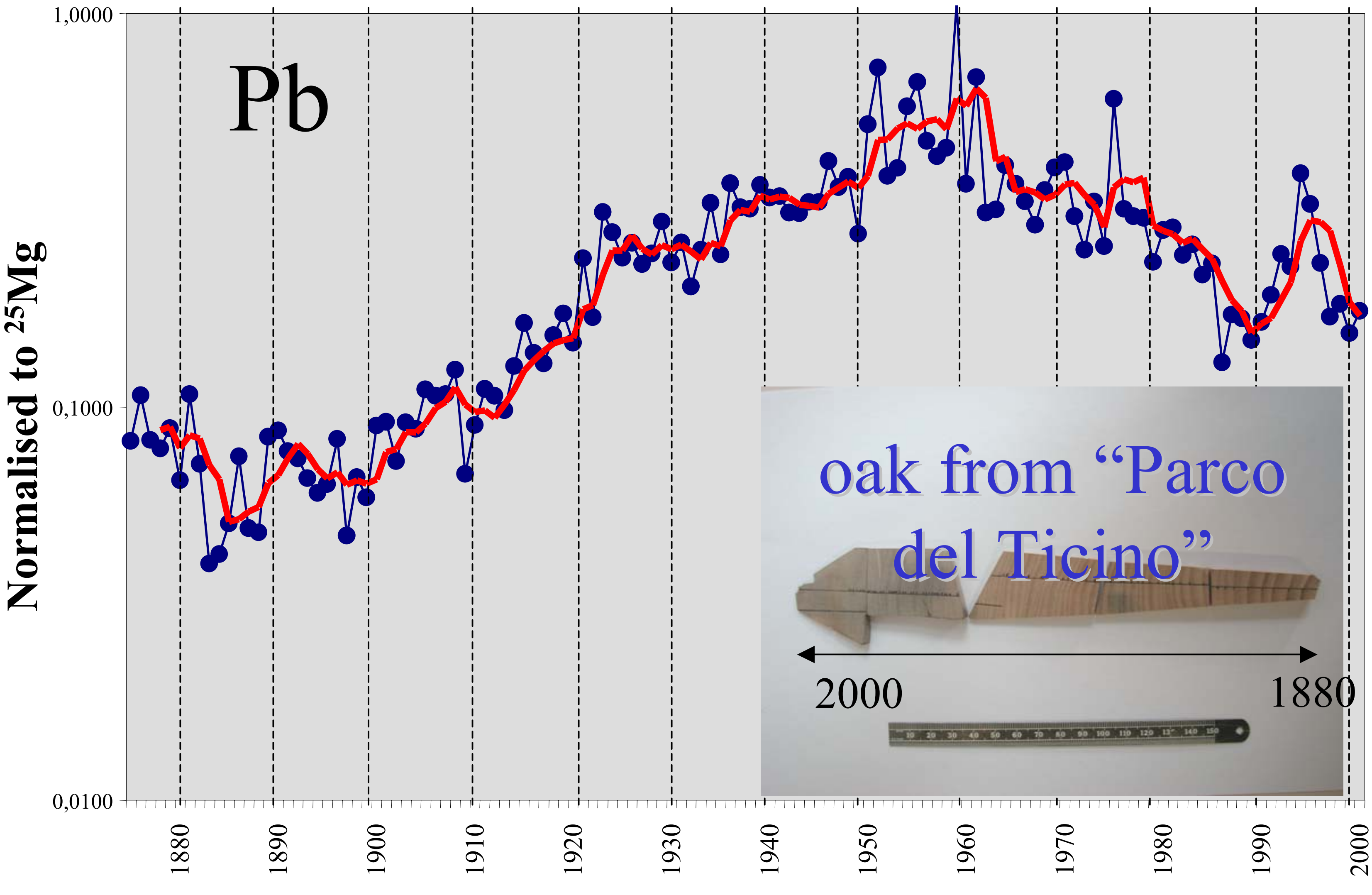


Clinopyroxene from forearc peridotites from Western Pacific Ocean

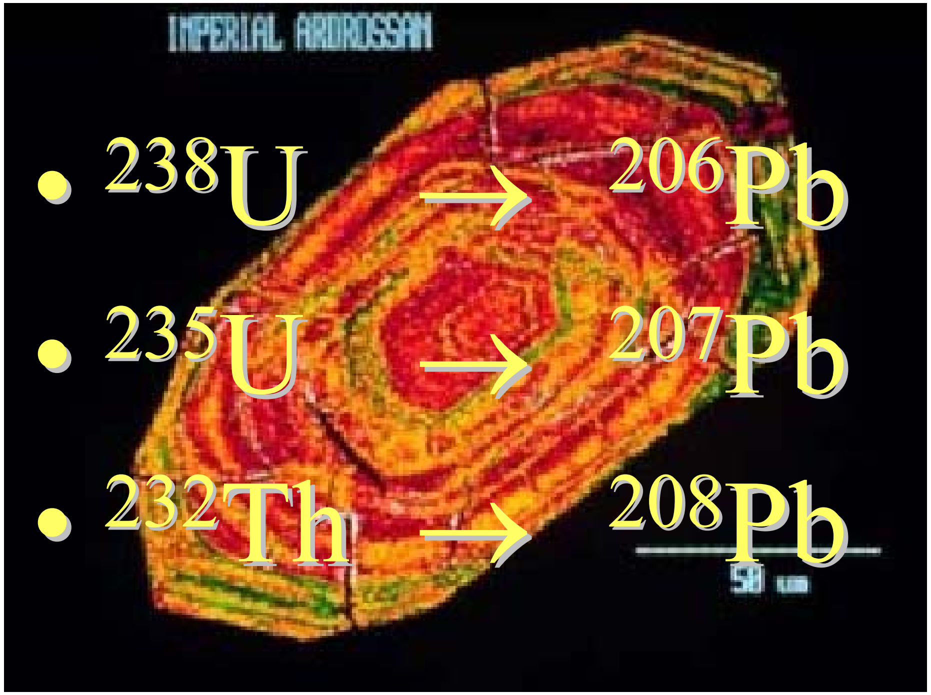
APPLICATIONS:
2) Human and animal bones



APPLICATIONS:
3) Tree rings



U-Th-Pb Geochronology
(LA)-HR-ICP-MS



- $^{238}U \rightarrow {}^{206}Pb$
- $^{235}U \rightarrow {}^{207}Pb$
- $^{232}Th \rightarrow {}^{208}Pb$

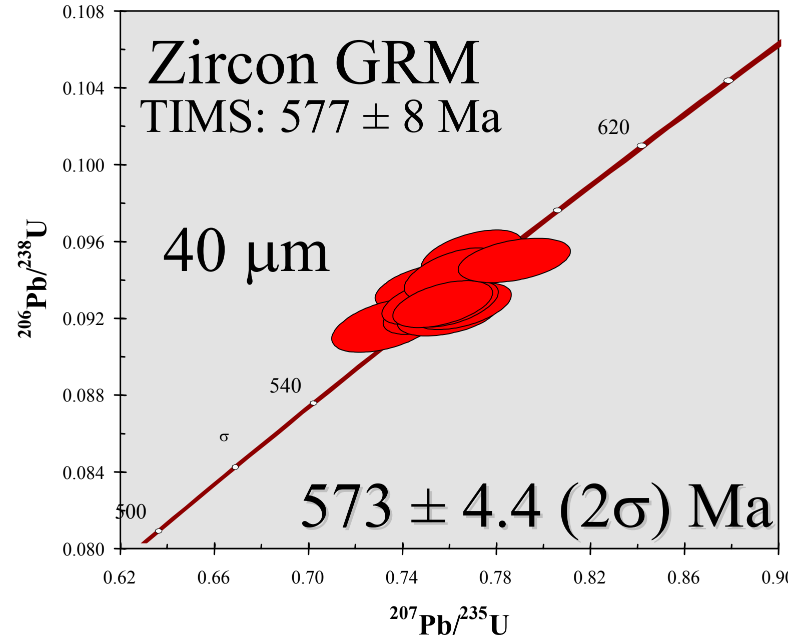
Zircon – Monazite

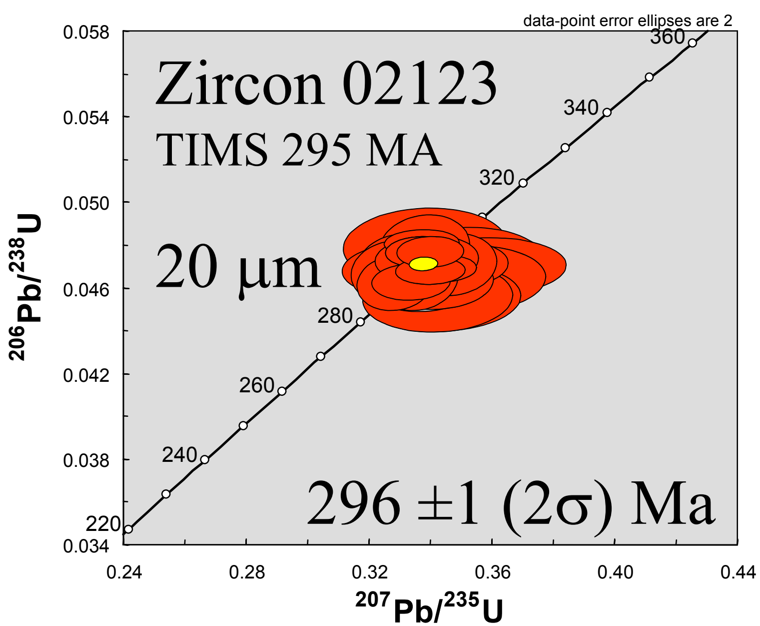
Zircon – 213 nm

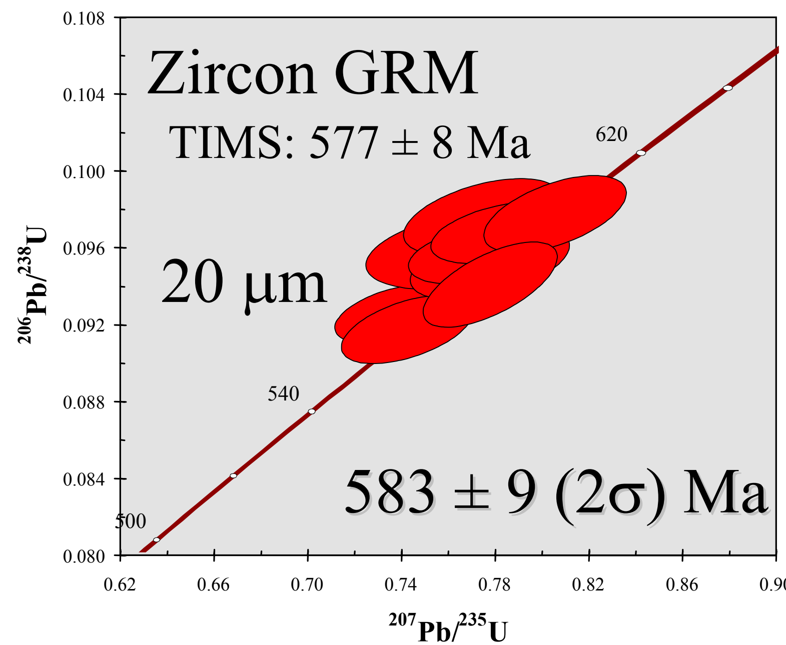
On single age determinations:

40 µm
Internal precision (2σ) : 1.0%

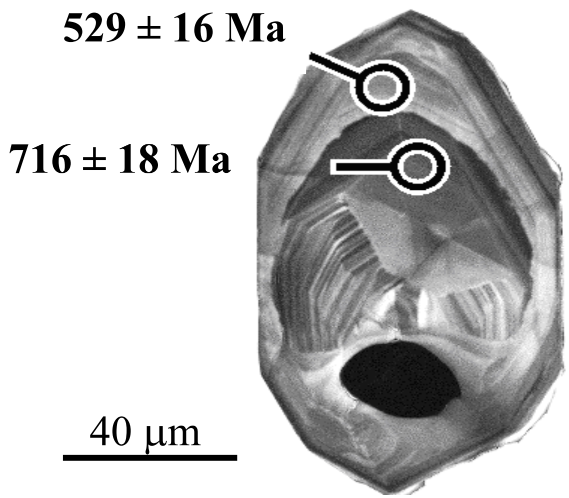
20 µm
Internal precision (2σ) : 1.5%



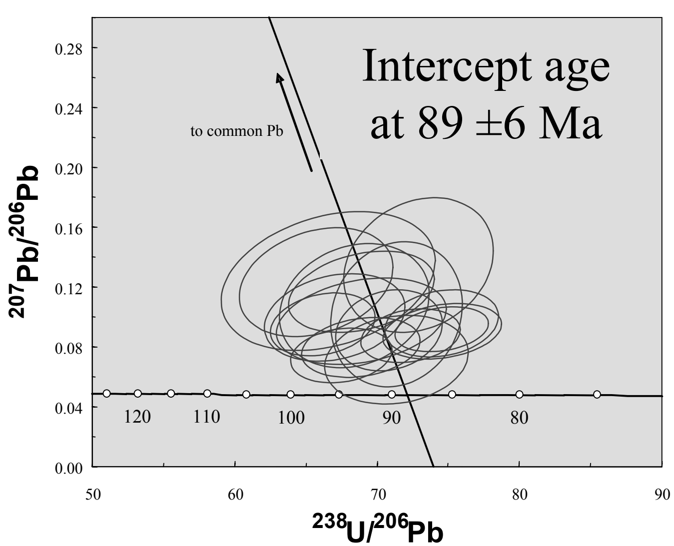




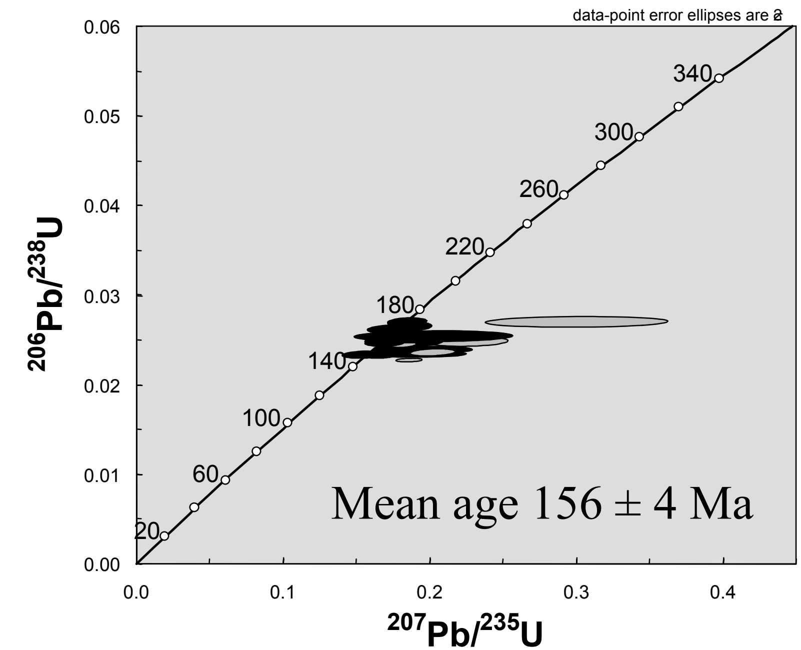
Zircons with inherited components

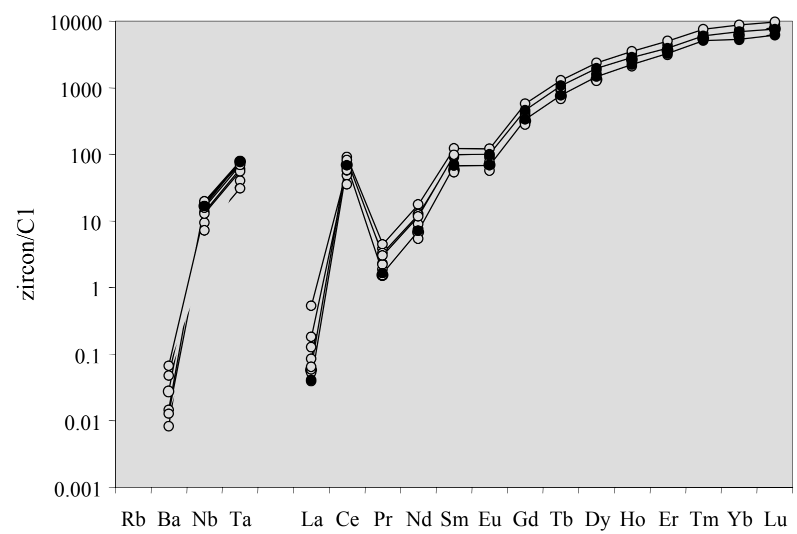


Antampombato-Ambatovy intrusion
(Madagascar)

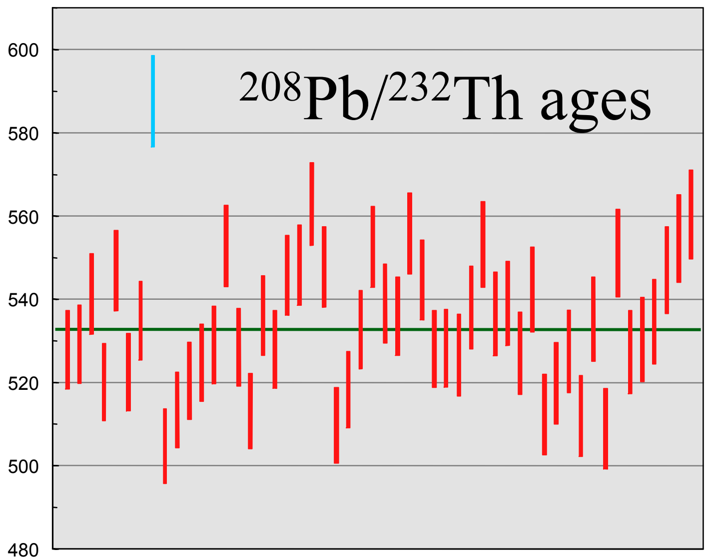


Internal Liguride ophiolites
(Northern Apennine, Italy)





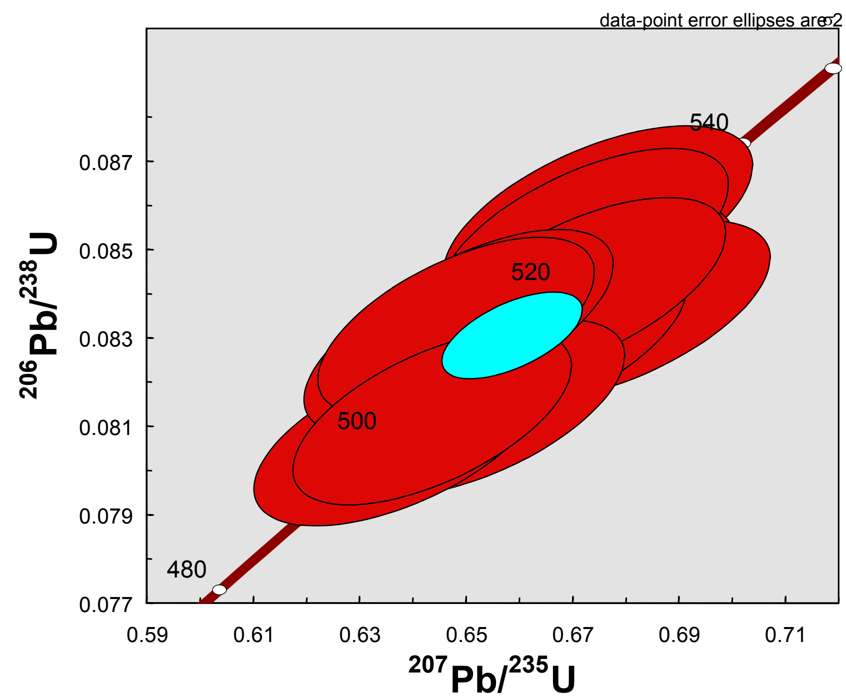
Monazite – 193 ArF Excimer laser
5 µm spot size



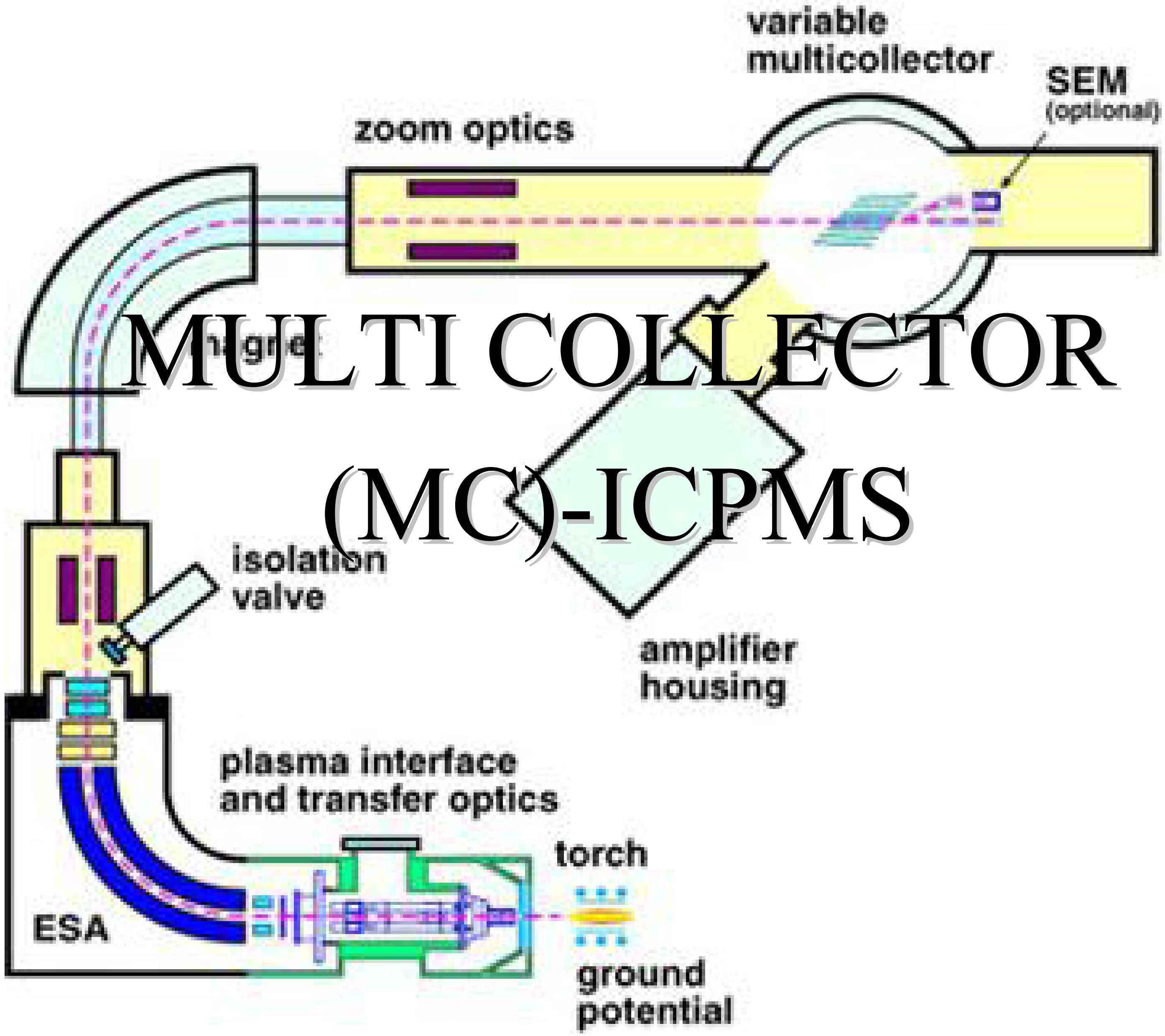
Mean $^{208}Pb/^{232}Th$ age
532.8 ± 4.0
[0.76%] 95% conf.

TIMS Age on zircons: 540 Ma

Concordia Age
514.2 ±3.8 Ma
(95% conf.)



MULTI COLLECTOR (MC)-ICPMS

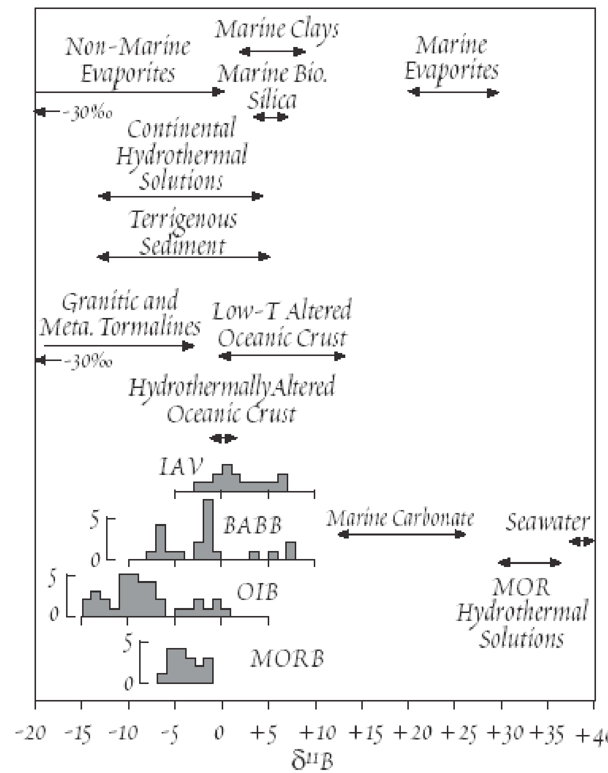


$^{11}B/^{10}B$ ratios

$\delta^{11}B‰=[(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{SRM951})-1]X1000)$

Major impediments in measuring $\delta^{11}B$ with Laser ablation MC-ICP-MS:

- ICP-MS
  - Low sensitivity for light masses
  - Faraday detectors require several hundreds ppm B in the sample for a precise $^{11}B/^{10}B$ determination under laser ablation
- B concentration
  - With the exception of a few minerals (e.g. tourmaline), B abundance is usually below 100 ppm and even below 1 ppm in mantle environments.
- Availability of standards



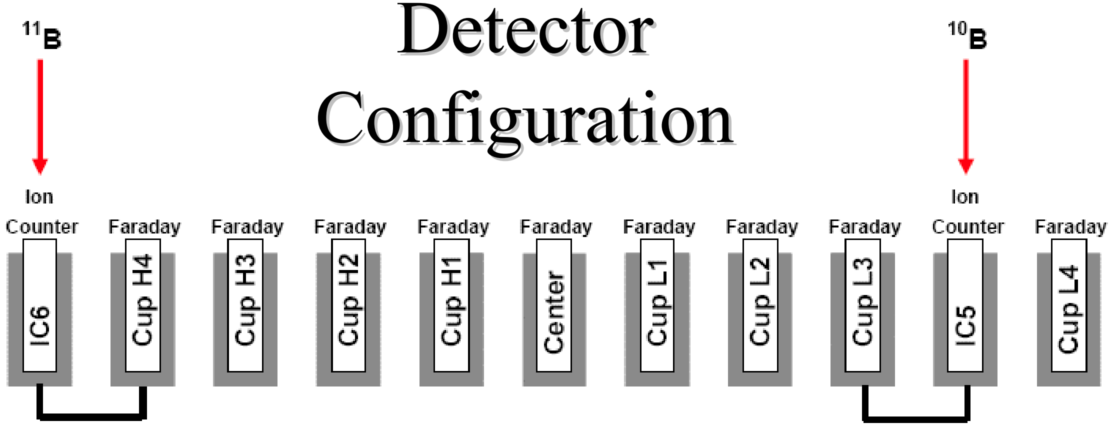
The LA-MC-ICP-MS instrument

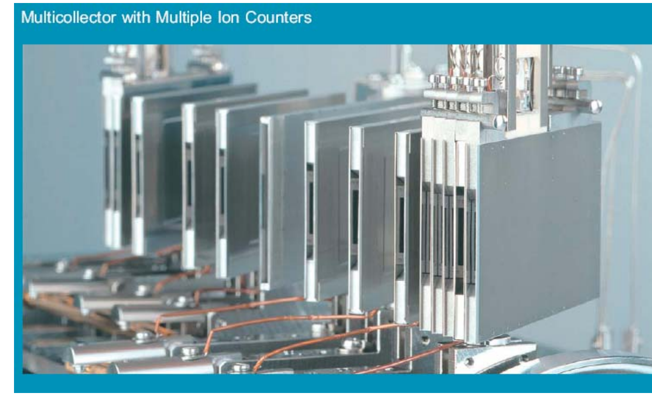
- Laser ablation system
  - Commercial UP213 from NewWave working at 213 nm.
  - The laser was operated in single spot mode with a repetition rate of 10 Hz and a spot size from 60 to 80 μm in diameter.

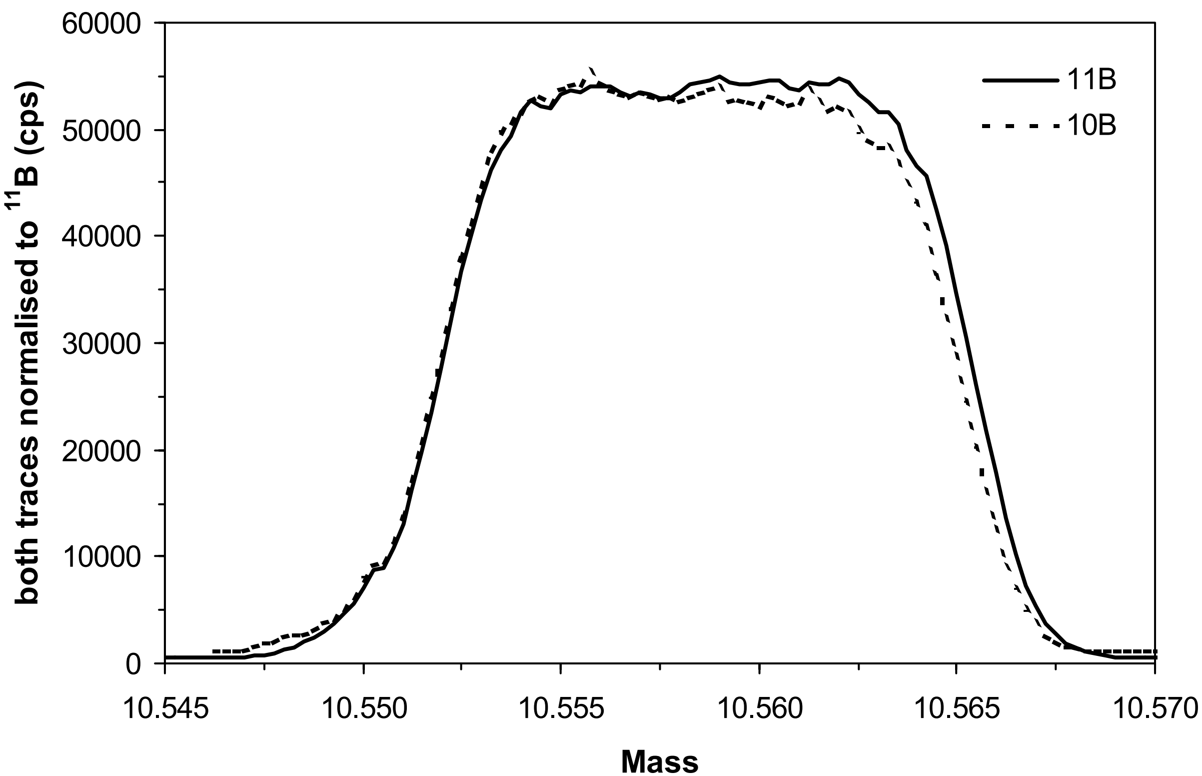
- MC-ICP-MS
  - The Finnigan Neptune (Thermo),
  - Equipped with both multiple ion counters and Faraday cups.

	B (ppm)	Reference	$\delta^{11}B$	2σ	Reference
NIST SRM 610	351-363	Kasemann et al. (2001) NIST website	-0.16 / -0.36	0.21 / 0.06	le Roux et al. (2004)
B4 tourmaline	31400	Gonfiantini et al. (2003)	-8.71	0.18	Tonarini et al. (2003)
StHs6/80-G	11.6, 12.5	Jochum et al. (2000) Rosner and Meixner (2004)	-4.48	0.29	Rosner and Meixner (2004)
GOR128-G	22.7, 21.8	Jochum et al. (2000) Rosner and Meixner (2004)	+13.55	0.21	Rosner and Meixner (2004)
GOR132-G	17.8, 15.6	Jochum et al. (2000) Rosner and Meixner (2004)	+7.11	0.97	Rosner and Meixner (2004)

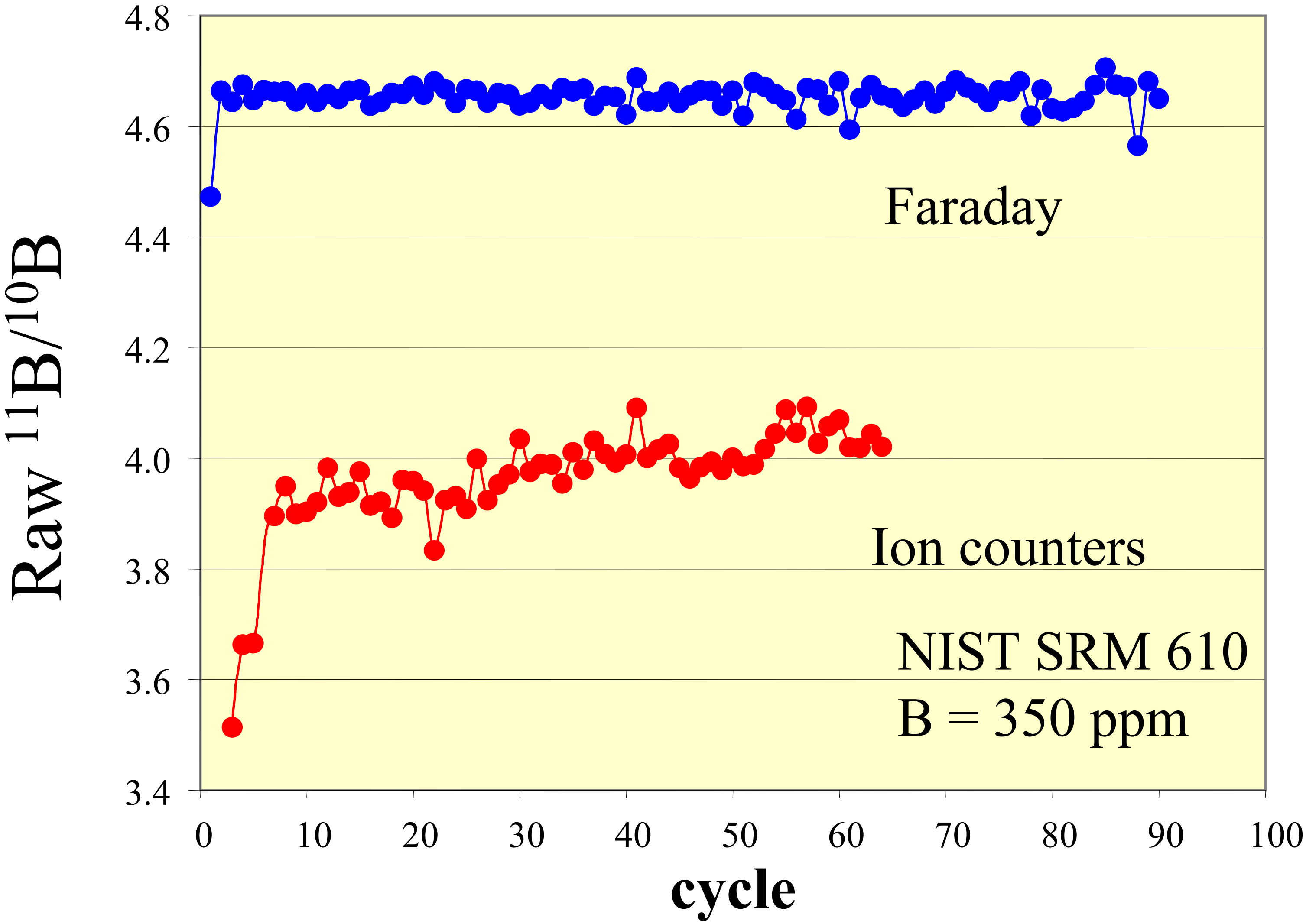
Detector Configuration





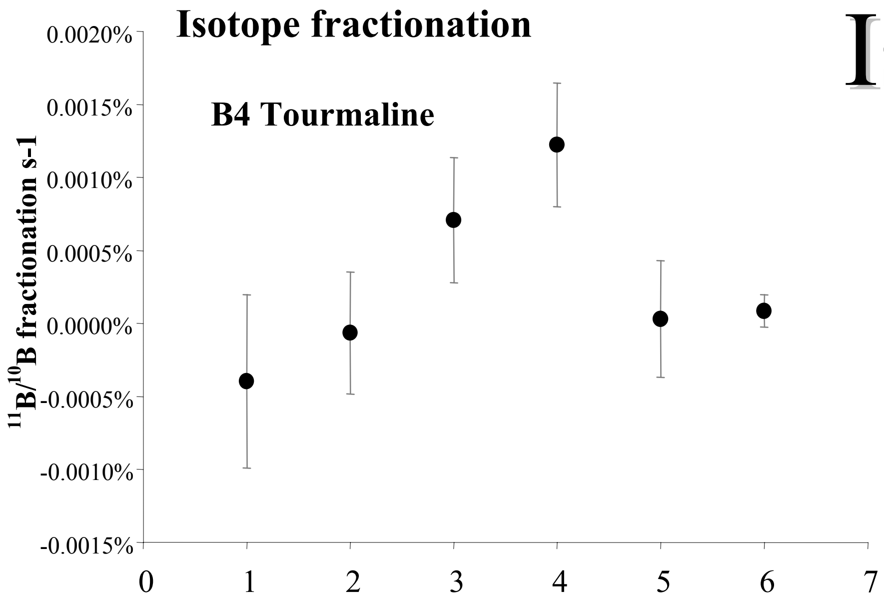


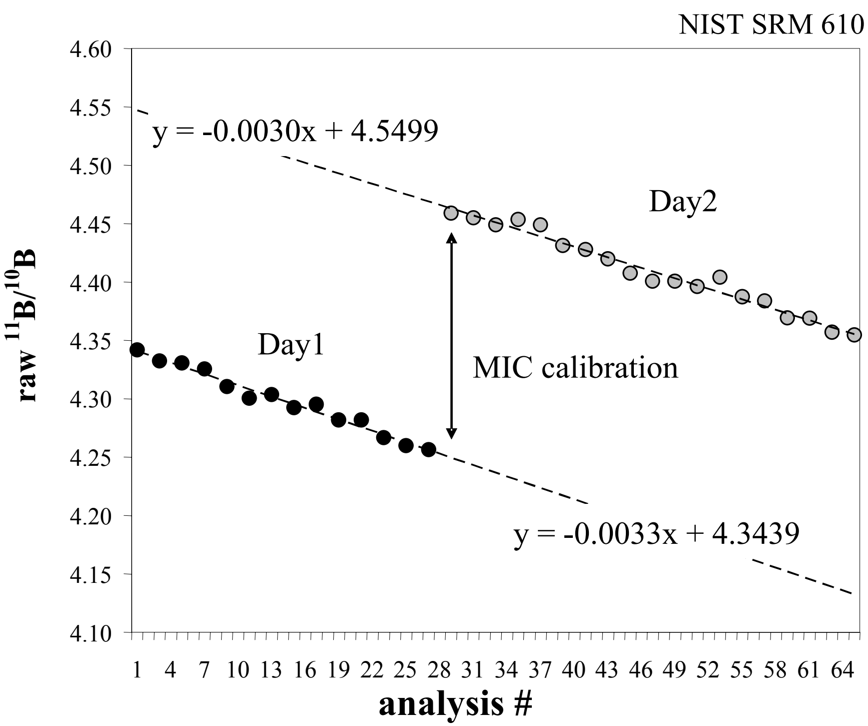
$^{11}B/^{10}B$ acquisition

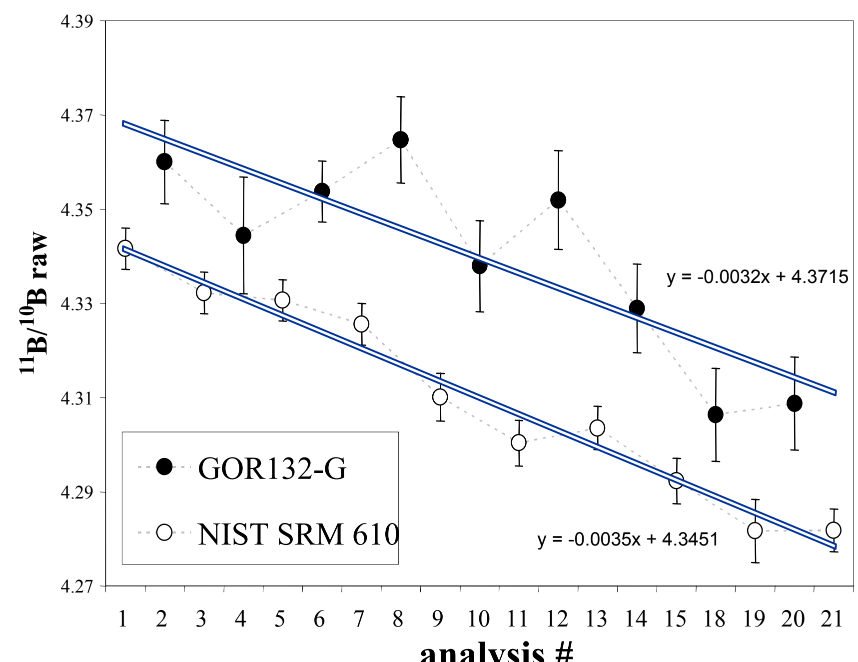


Isotope Fractionation

1. Instrumental Mass bias (13-14%)
2. Laser induced fractionation
3. Drift of detector (MIC)







Analytical Method

Correction of:

Mass bias – laser induced isotopic fractionation – ion counter drift

$$\left({}^{11}B/{}^{10}B\right)^{corrected}_{unknown} = \frac{\left({}^{11}B/{}^{10}B\right)^{measured}_{unknown}}{\dfrac{\left({}^{11}B/{}^{10}B\right)^{measured1}_{NIST610} + \left({}^{11}B/{}^{10}B\right)^{measured2}_{NIST610}}{2} \times \dfrac{1}{\left({}^{11}B/{}^{10}B\right)^{accepted}_{NIST610}}}$$

standard → sample → standard → sample → standard →

External standard Nist 610 – $^{11}B/^{10}B = 4.0490$

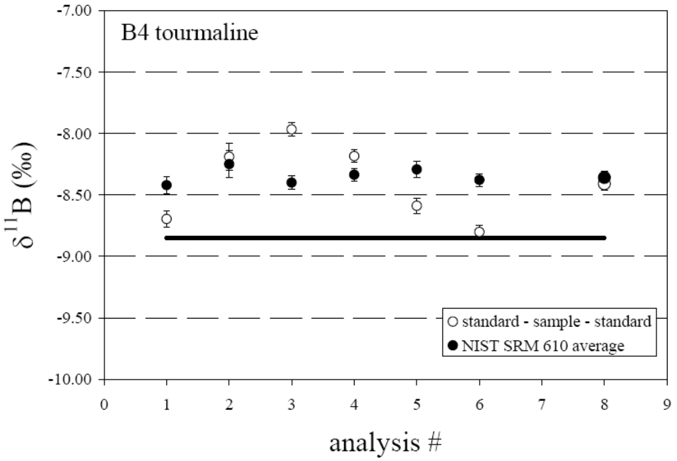
(le Roux et al., 2004)

Faraday – B4 tourmaline and Nist 610

Sample	$^{11}B/^{10}B_{meas}$	sd	r.s.d.
Nist610	4.6833	0.0027	0.058%
B4	4.6268	0.0001	0.003%
Nist610	4.6662	0.0025	0.053%
B4	4.6276	0.0002	0.005%
Nist610	4.6631	0.0022	0.048%
B4	4.6269	0.0001	0.002%
Nist610	4.6627	0.0024	0.052%
B4	4.6272	0.0001	0.002%
Nist610	4.6657	0.0021	0.046%
B4	4.6274	0.0001	0.003%
Nist610	4.6669	0.0025	0.053%
B4	4.6270	0.0001	0.002%
Nist610	4.6551	0.0020	0.043%
Averages			
B4	**4.6272**	**0.00031**	**0.007%**
Nist610	**4.6649**	**0.00191**	**0.041%**

B4 = 31400 ppm B

Nist610 = 350 ppm B



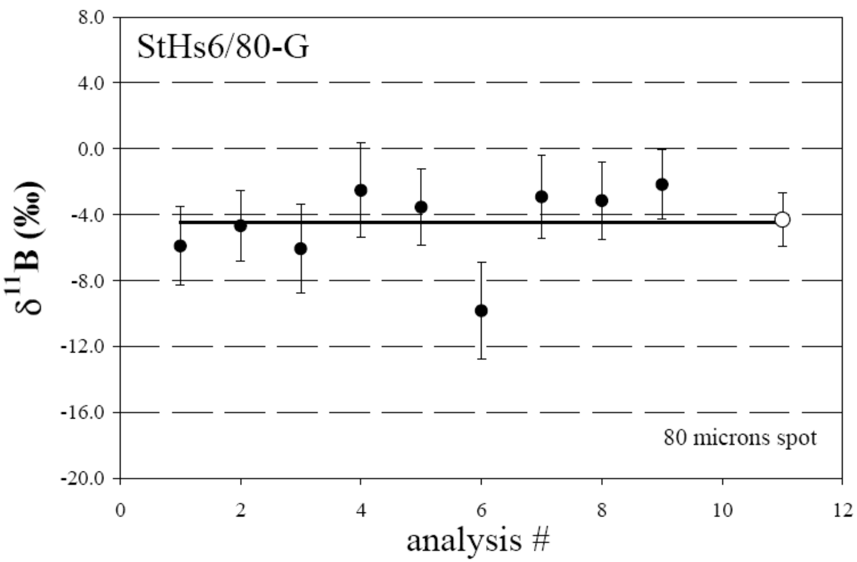
$\delta^{11}B = 8.41 \pm 0.34‰$

Multi Ion Counters – StHs6/80

Sample	$^{11}B/^{10}B_{meas}$	sd	r.s.d.
Nist610	4.3839	0.0051	0.12%
StHs	4.3491	0.0096	0.22%
Nist610	4.3638	0.0052	0.12%
StHs	4.3430	0.0088	0.20%
Nist610	4.3608	0.0038	0.09%
StHs	4.3312	0.0109	0.25%
Nist610	4.3523	0.0060	0.14%
StHs	4.3434	0.0116	0.27%
Nist610	4.3543	0.0046	0.11%
StHs	4.3399	0.0094	0.22%
Nist610	4.3542	0.0048	0.11%
StHs	4.3054	0.0119	0.28%
Nist610	4.3399	0.0066	0.15%
StHs	4.3250	0.0103	0.24%
Nist610	4.3332	0.0052	0.12%
StHs	4.3159	0.0096	0.22%
Nist610	4.3237	0.0050	0.11%
StHs	4.3230	0.0084	0.20%
Nist610	4.3389	0.0044	0.10%

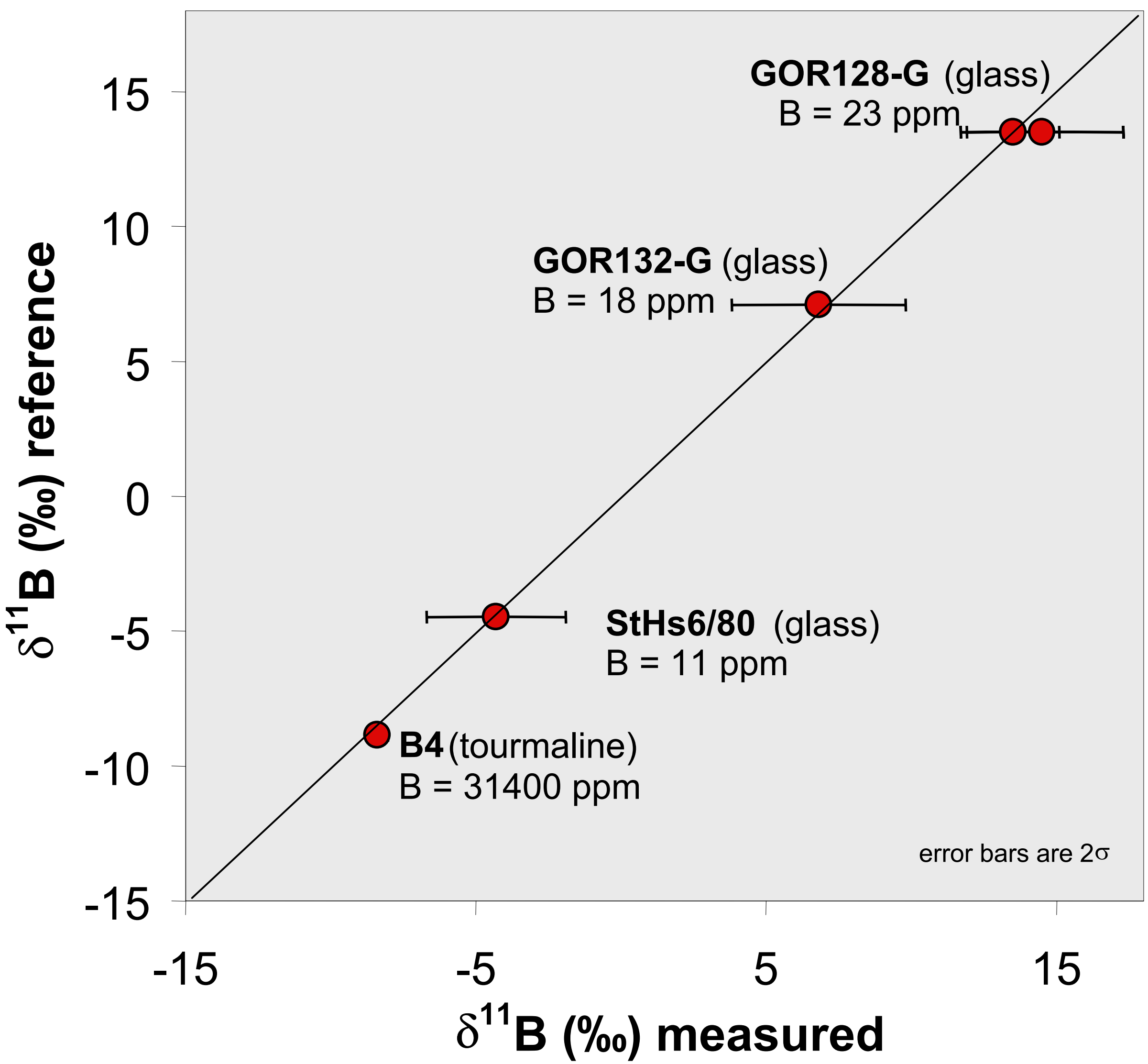
StHs6/80= 12 ppm B

Nist 610 = 350 ppm B

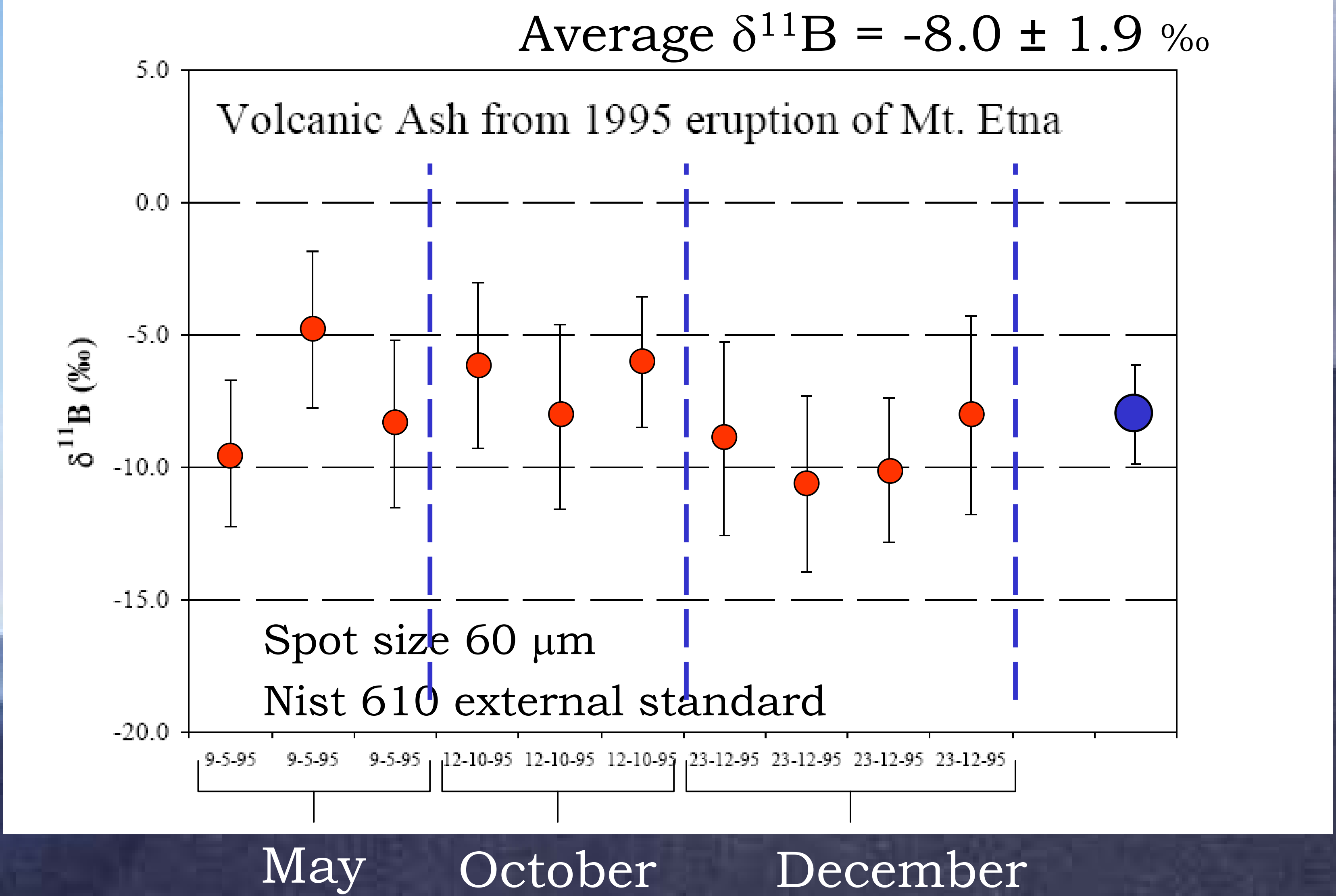


$\delta^{11}B = -4.3 \pm 2.4‰$

Summary of results



Results on Mt. Etna ashes



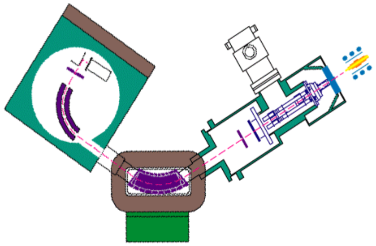
Other possible applications

- High precision U-Pb zircon dating
- Li, Hf, Pb, Sr isotopes on geological samples

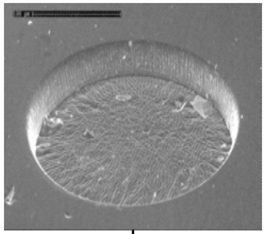
Provided that suitable standards for in-situ analyses are available

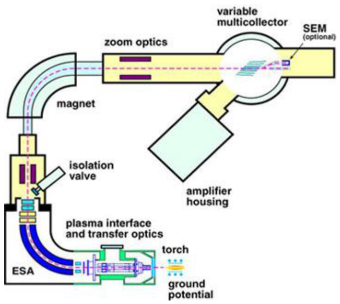
Conclusions

Laser Ablation microprobe
(266/213/193 nm)



(LA)





MC-ICPMS

High precision isotope determinations

Ion counters
(ppm level determinations)

Faraday
(100s ppm determinations)

HR-ICPMS

Multi element
(ppb level LOD)
&
low precision isotope determinations
(Pb-geochronology)