Laser Induced Breakdown Spectroscopy (LIBS)

Fernando Rull Perez

•Unidad Asociada UVA-CSIC al Centro de Astrobiología. Universidad de Valladolid.
•Parque Tecnológico de Boecillo. E47145-Valladolid, SPAIN ,

Universidad de Valladolid

Centro de Astrobiología

Consejo Superior de Investigaciones Científicas

Instituto Nacional de Técnica Aerospacial

NASA Astrobiology Institute

Motivation

LIBS share many of the advantages previously claimed for Raman

No sample preparation is needed

Very fast acquisition data

Micro-macro modes

Contac-remote modes

Laser ablation allows to perform dust removal in the samples and also to analyze layer by layer from the surface the samples

Capability to combine with other techniques in a single instrument

LIBS is a partially (micro to local) destructive technique because needs to provoke a plasma in the target

LIBS principles

Laser Induced Breakdown Spectrometry (LIBS)

Different names for an unique technique :

Laser Induced Breakdown Spectrometry (LIBS)

Laser Induced Plasma Spectrometry (LIPS)

Time- Resolved LIBS (TRELIBS)

Laser Ablation Atomic Emission Spectrometry (LAES)

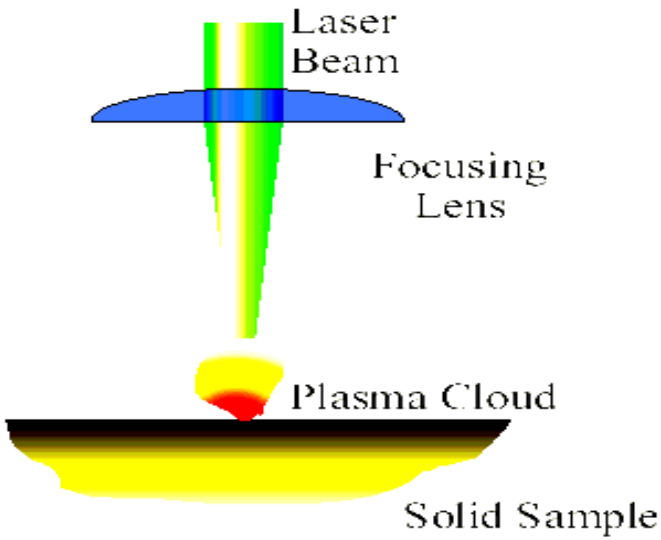
Laser Ablation Optical Emission Spectroscopy (LA-OES)

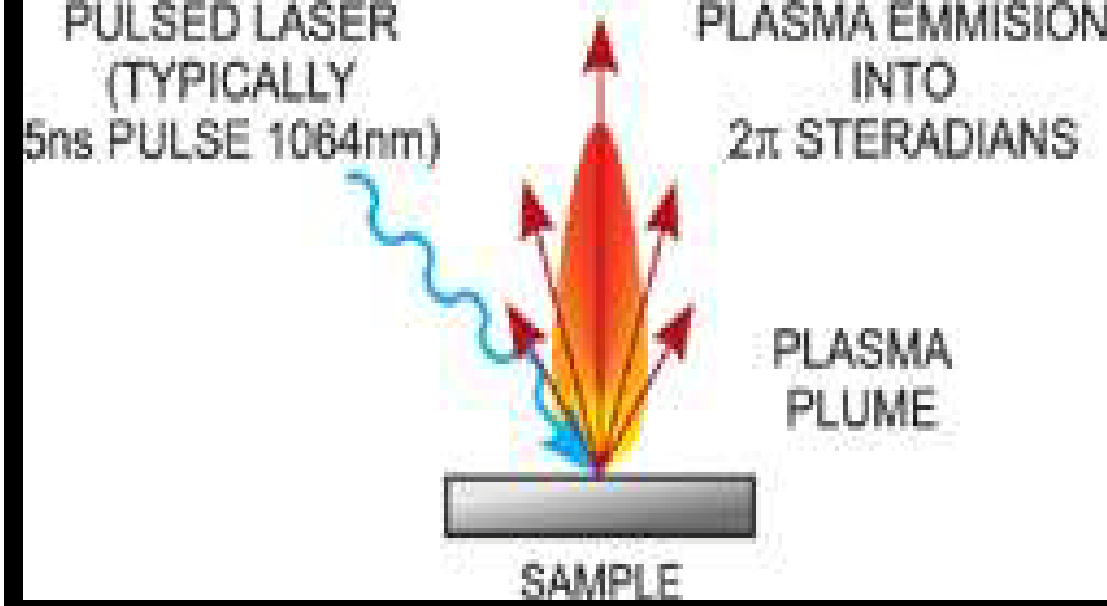
Laser Spark Emission Spectral Analysis (LIESA)

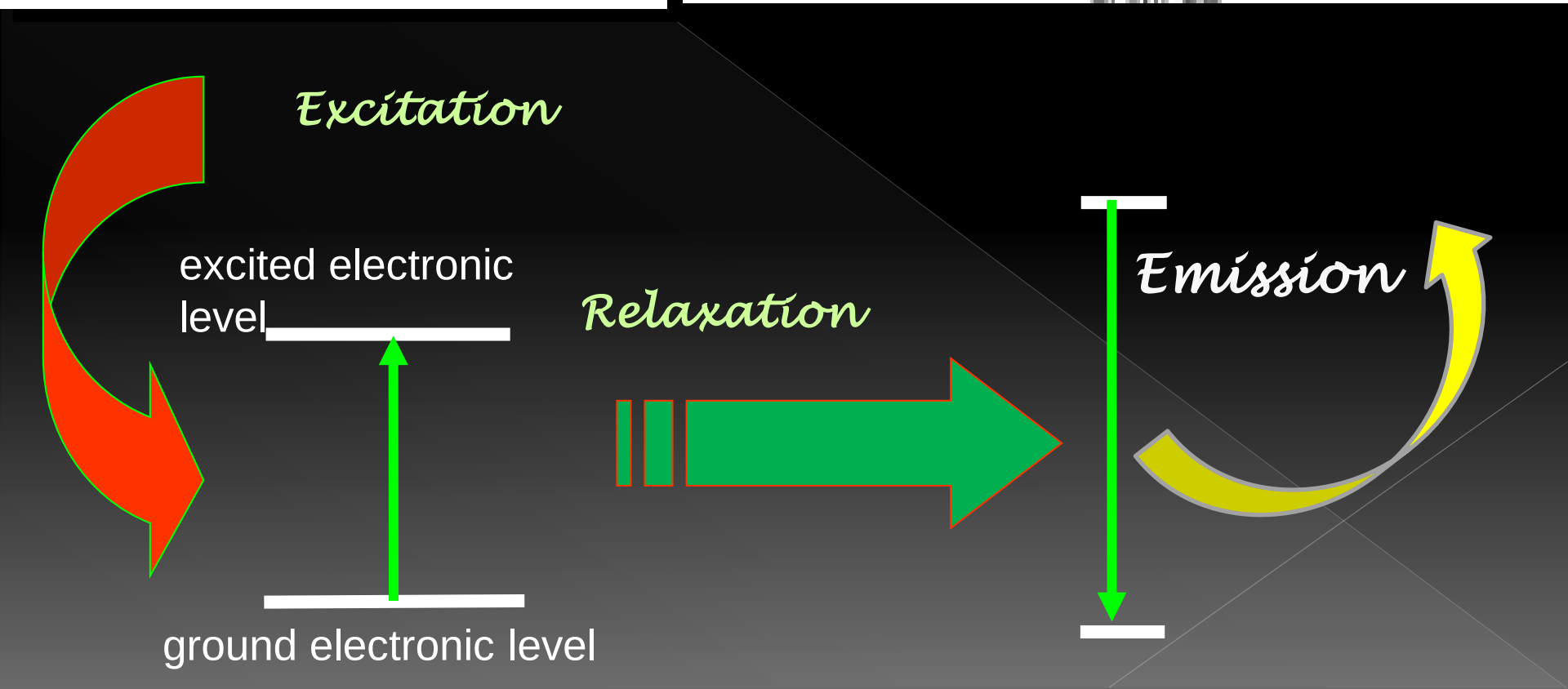
Laser Spark Spectroscopy (LASS)

LIBS History

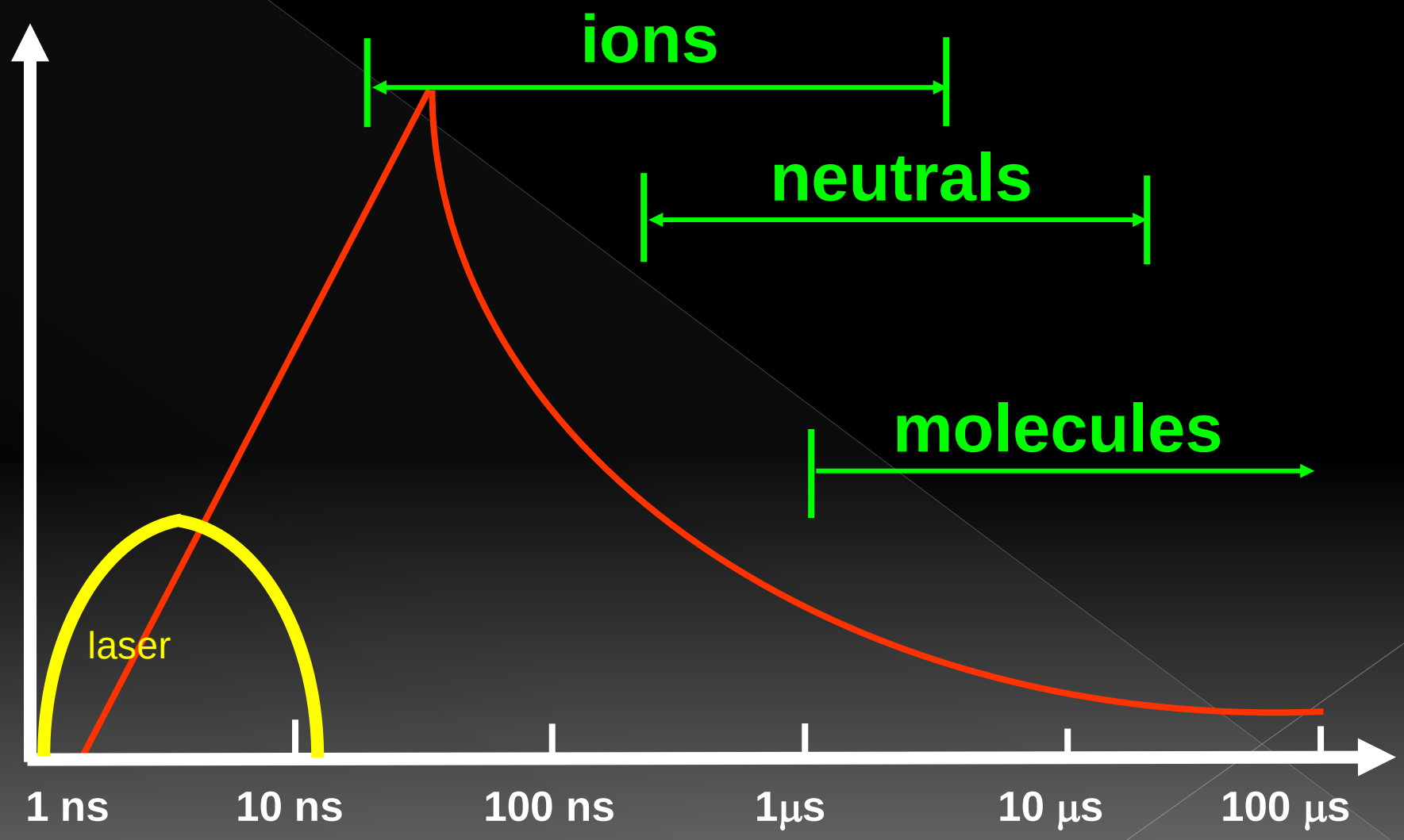
- Late 60s : 1st LIBS report (Brecht & Cross 1962)
- Early 70s : LIBS research continued to grow a peak in about 1970
- Early 80s : Research interest resurged in mid-1980s (due to availability to increasing reliable, smaller, less costly laser systems, and developement of ICCD)
- Since 1990 : Technology - driven renewed interest in analytical chemistry : development of field-portable instruments

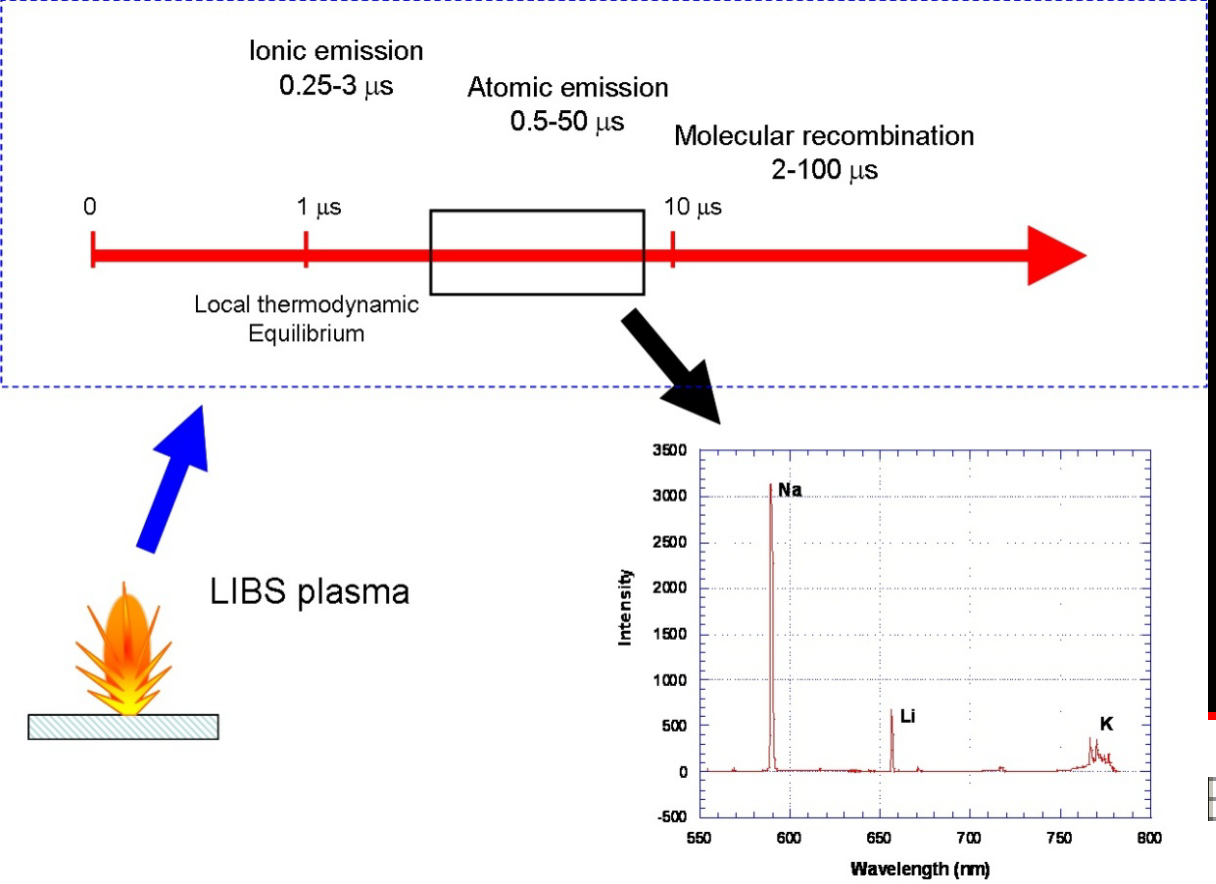

Laser
Beam
Focusing
Lens
Plasma Cloud
Solid Sample

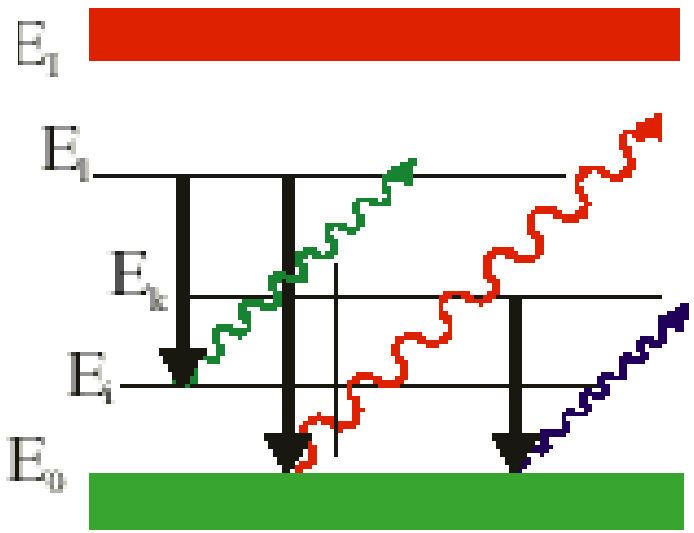

PULSED LASER
(TYPICALLY
5ns PULSE 1064nm)
PLASMA EMMISION
INTO
2π STERADIANS
PLASMA
PLUME
SAMPLE


Excitation
excited electronic
level
ground electronic level
Relaxation
Emission

The process is time-dependent





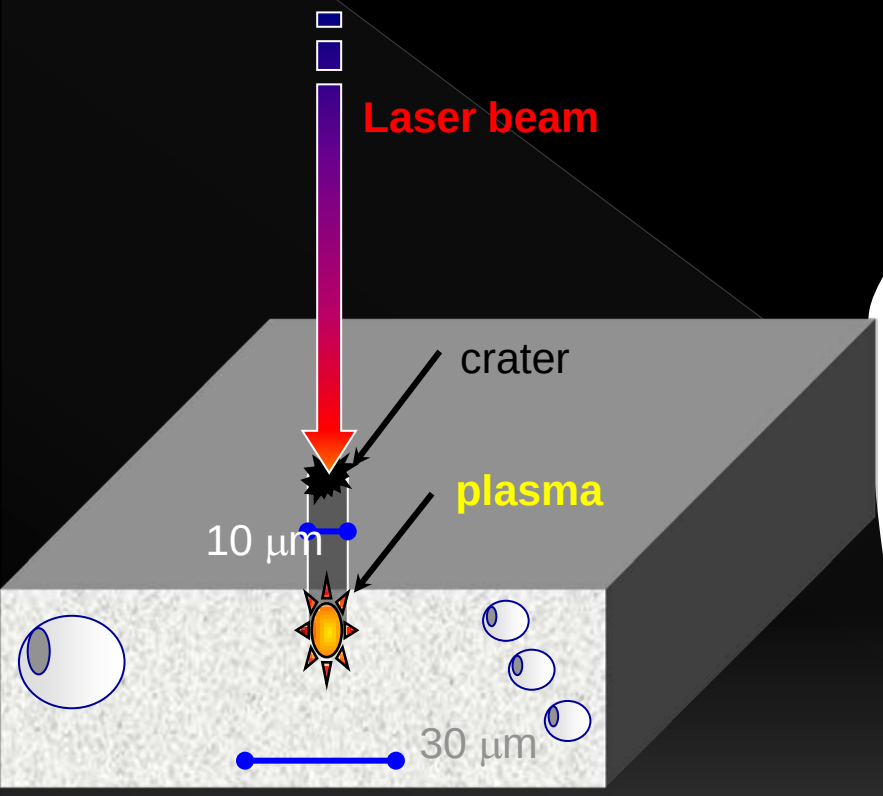


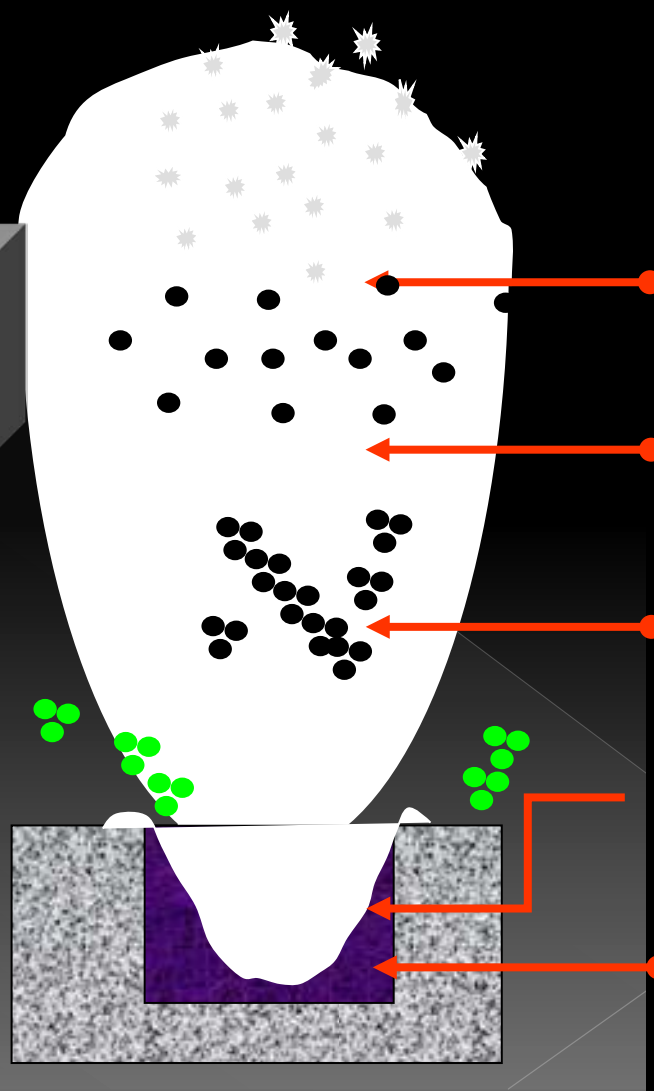
Optical emission

The excited atoms return to the fundamental electronic level : emission of radiations with different wavelengths or energy

Radiative electronic transitions

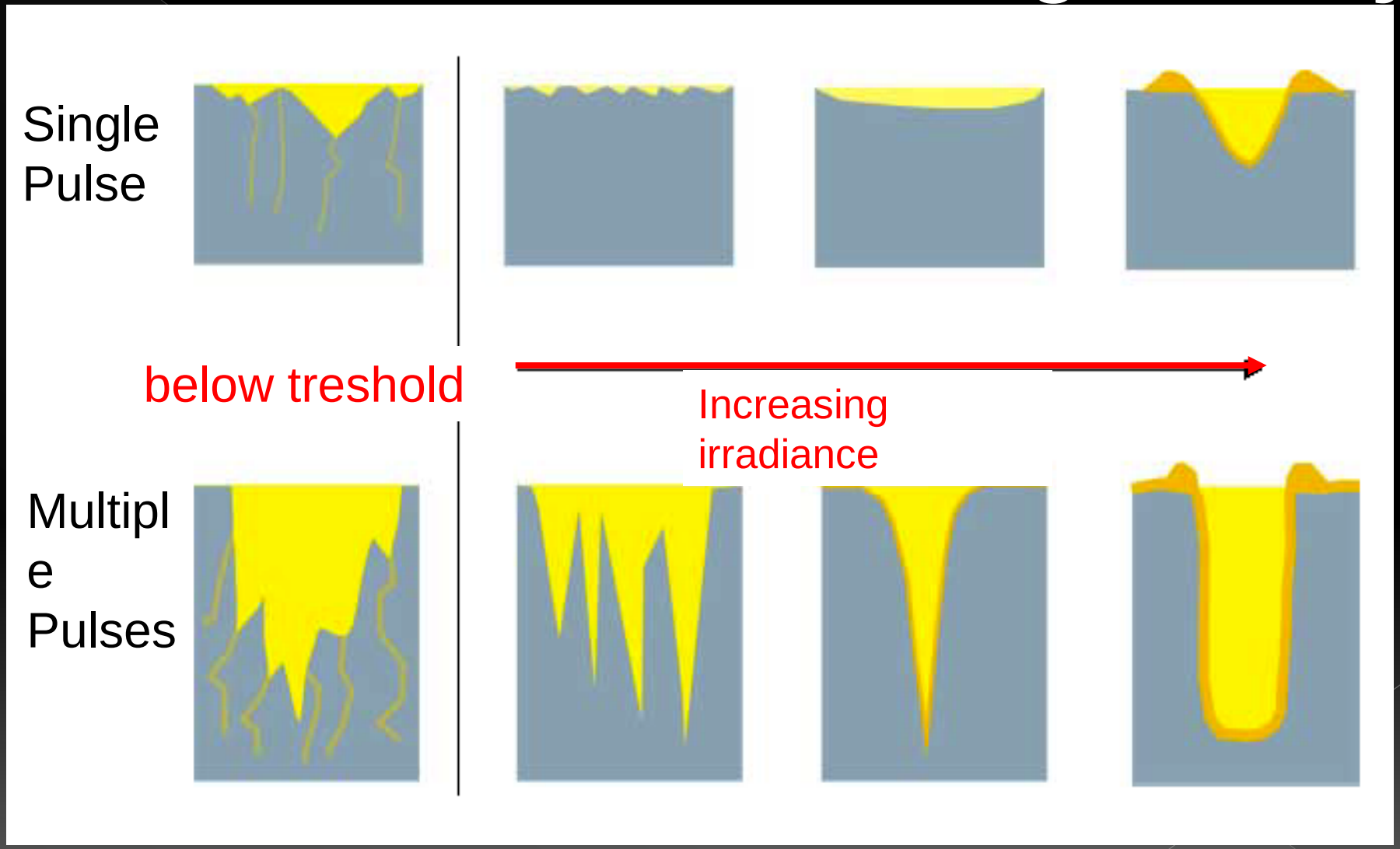
The ablation process



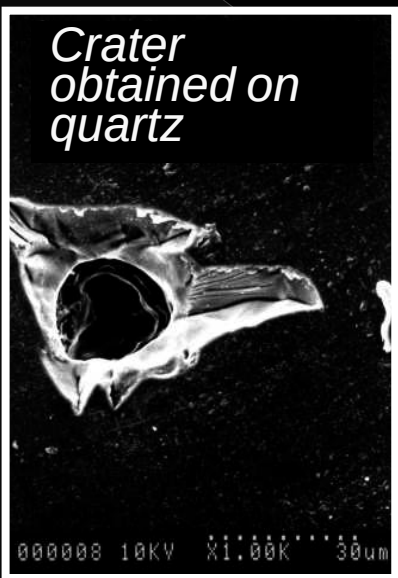


Plasma depends on atmospheric conditions

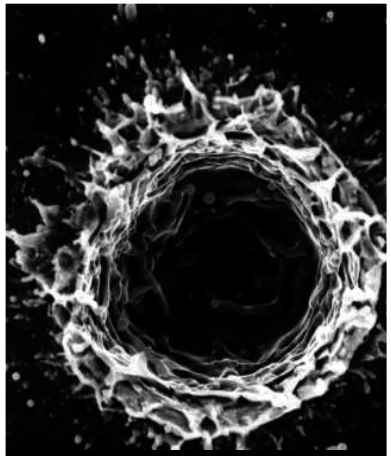
Laser-matter interaction: geometry



Spatial resolution



Crater obtained on quartz



Crater obtained on copper

Short laser pulse duration

and high speed ejection of the plasma

no significant thermal diffusion in the targe

Lateral resolution for macro-LIBS: 200 to 300 μm

for micro-LIBS : 8 μm down to

Depth profile dependent of the material:

from 0.1 μm to 6-8 μm per laser shot

Analytical Principle of LIBS

$$I_a = k.\ C_{sa}\ .\ P\ .\ S\ .\ \tau_{abl}\ .\ \tau_{atom}\ .\ \tau_{exc}\ .\ I_{ij}$$

I_a : analytical

k : instrumental factor

C_{sa} : concentration of element a in the solid

P: laser power

S : surface of interaction between laser and matter

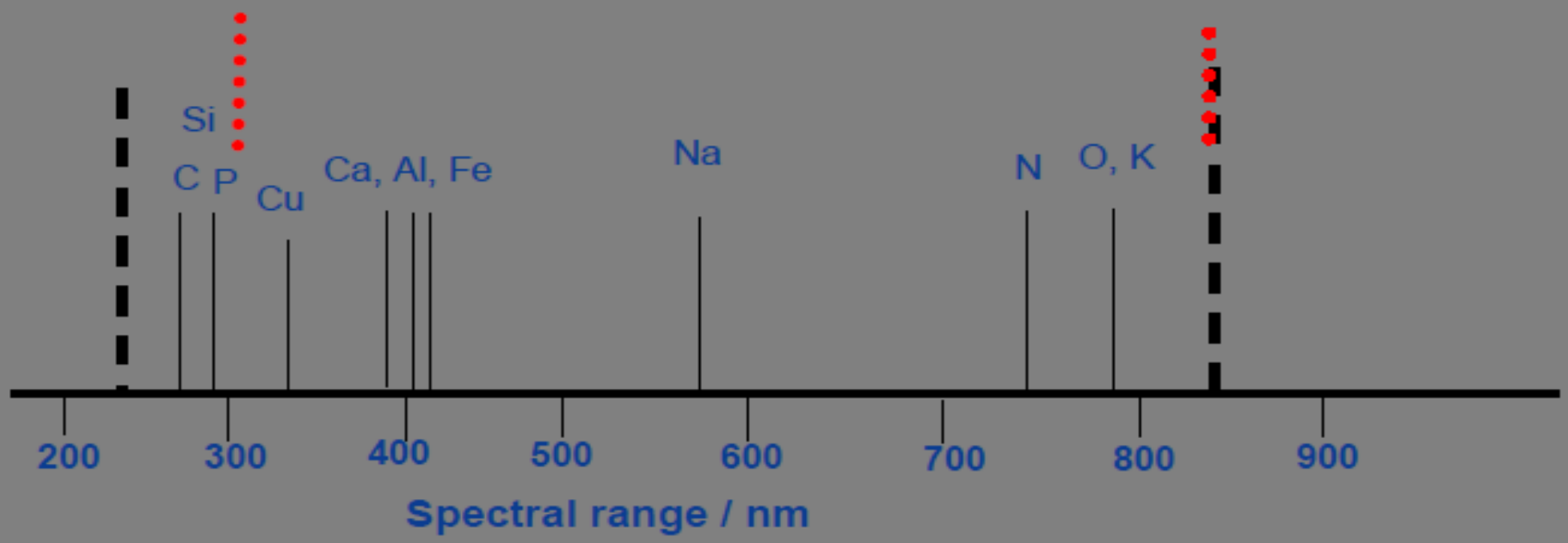
τ_{abl}: ablation yield

τ_{atom}: atomisation yield

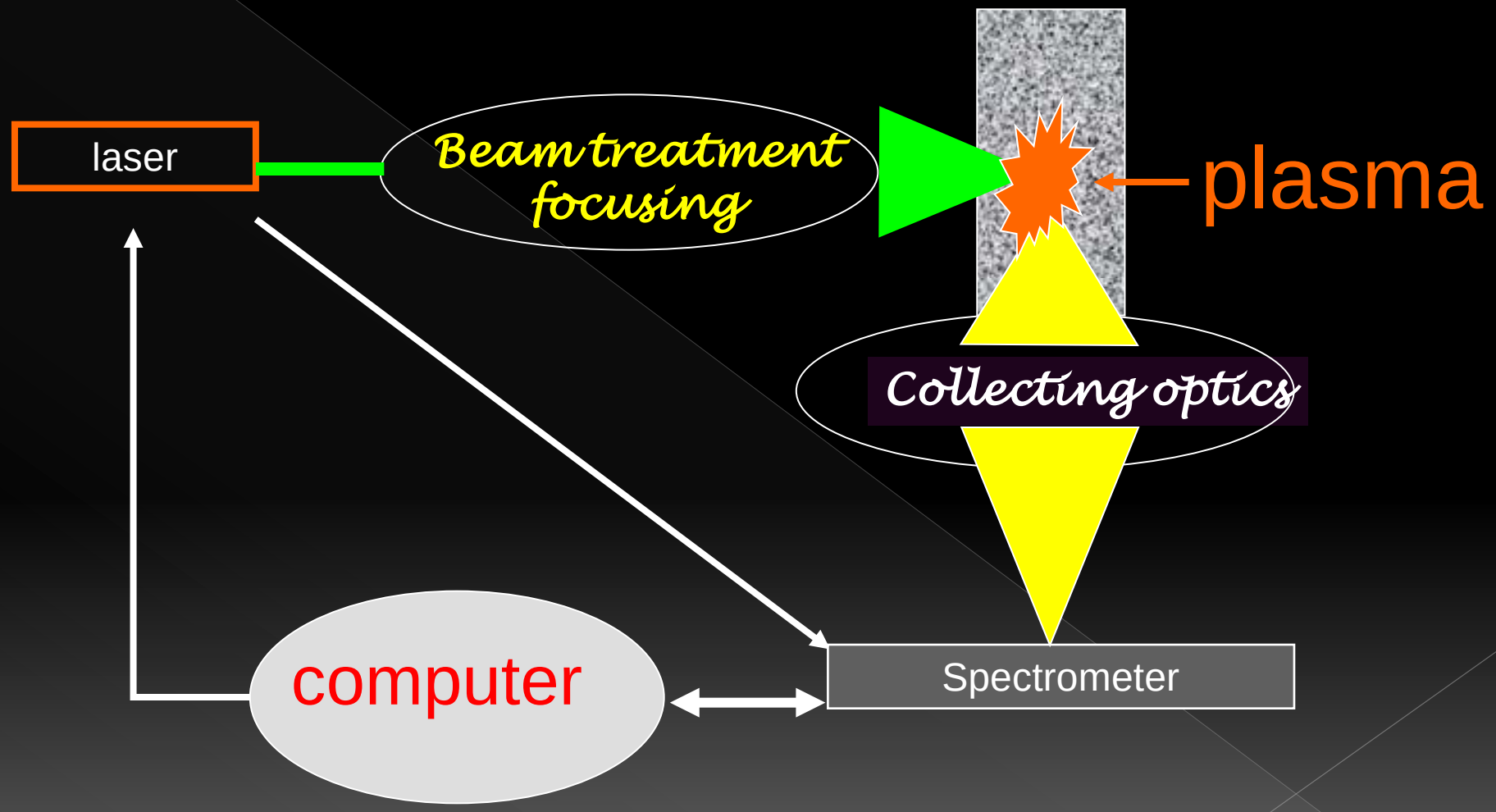
τ_{exc}: excitation yield

LIBS detection capability

Options	Elements you could measure with LIBS
RLS-A, -A1, -B 240 – 840 nm	O, Na, Mg, Al, Si, K, Ca, Ti, Fe H, Li, C, N, S, Cl, P, Mn, Ni, Cu, Sr, Ba
RLS-C >300 – 840 nm	O, Na, Mg, Al, Si, K, Ca, Ti, Fe H, Li, N, S, Cl, Mn, Sr, Ba
RLS-C1 535 – 740 nm	Na, Al, Si, Ca, Ti, Fe H, Li, N, S

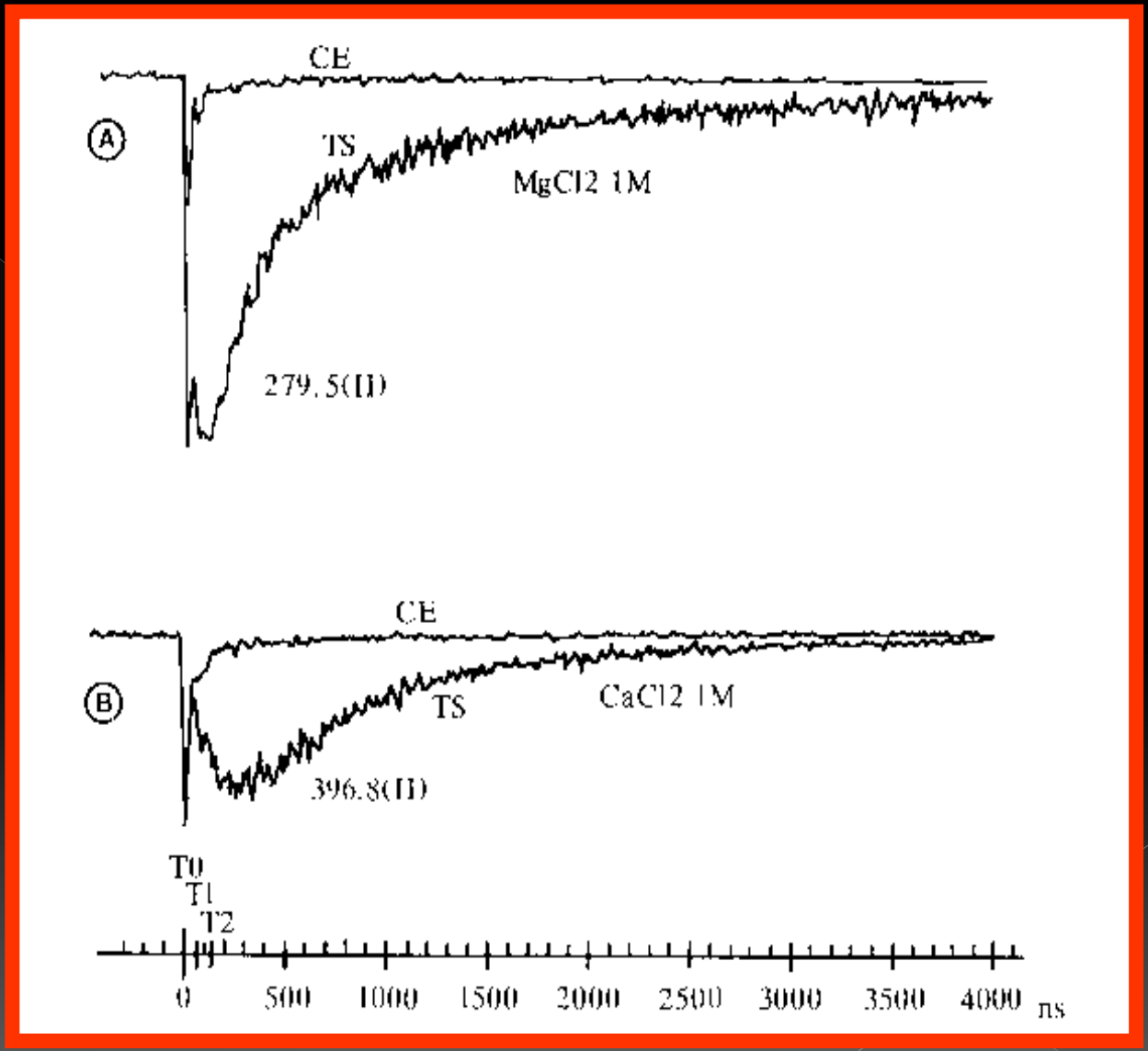


Instrumentation for LIBS



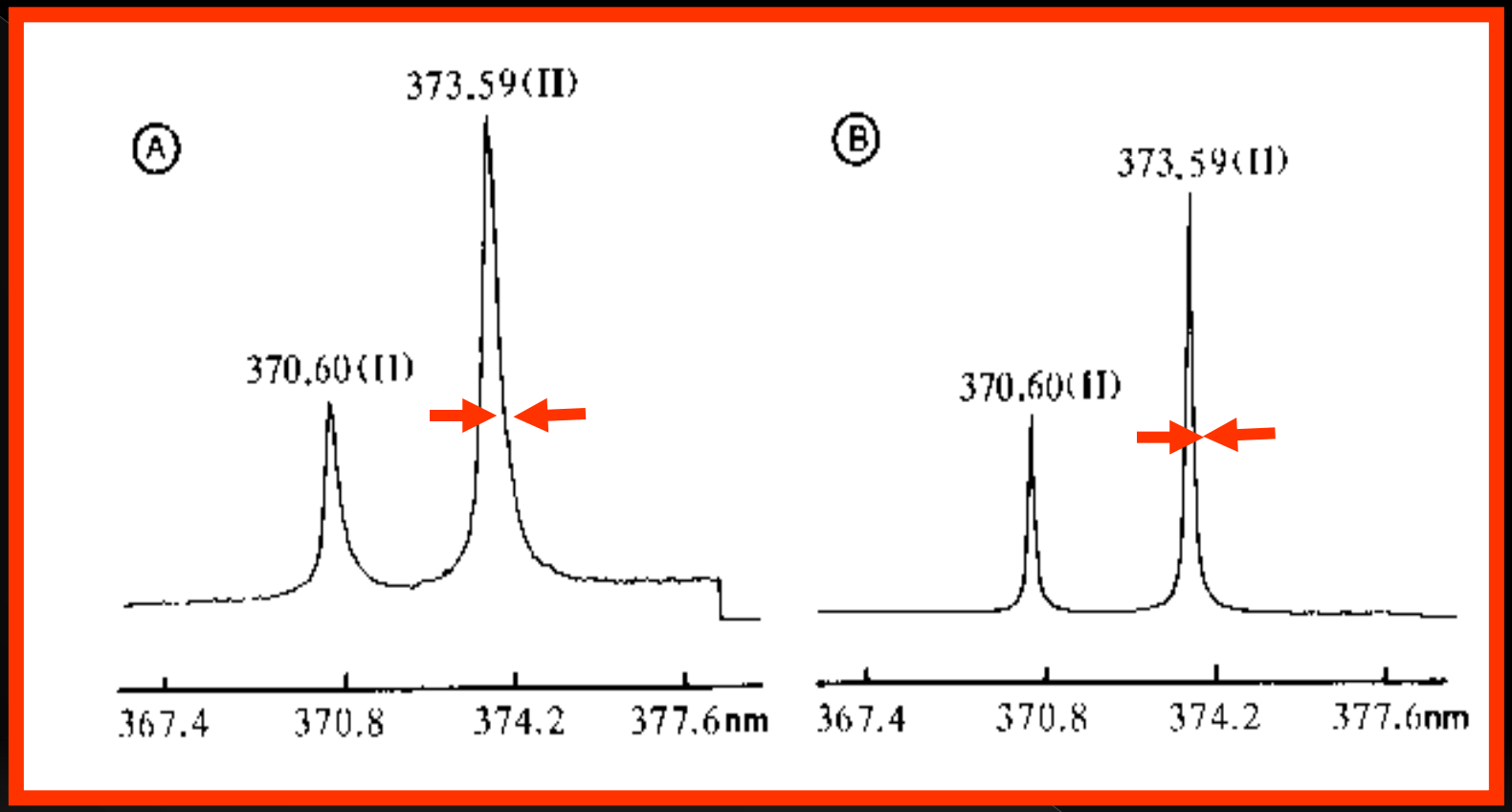
Specifications for the detection system

Evolution of the intensity of continuum and signal with time



Time resolution: delay (ns to ms) gate (.1μs to ms)

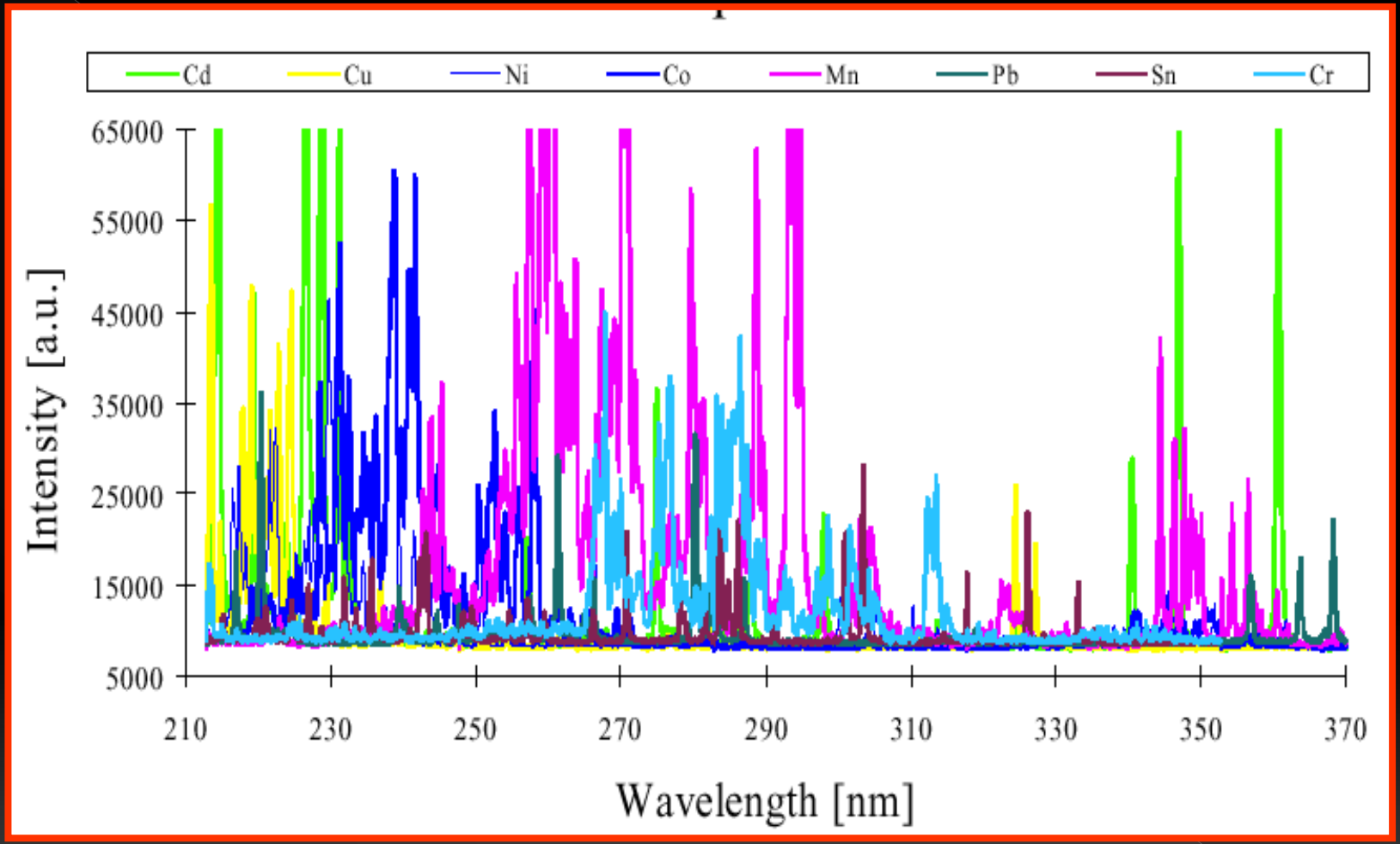
Specifications for the detection system



Evolution of the FWHM of emission lines with time

Time resolution: delay (ns to ms) gate (.1μs to ms)

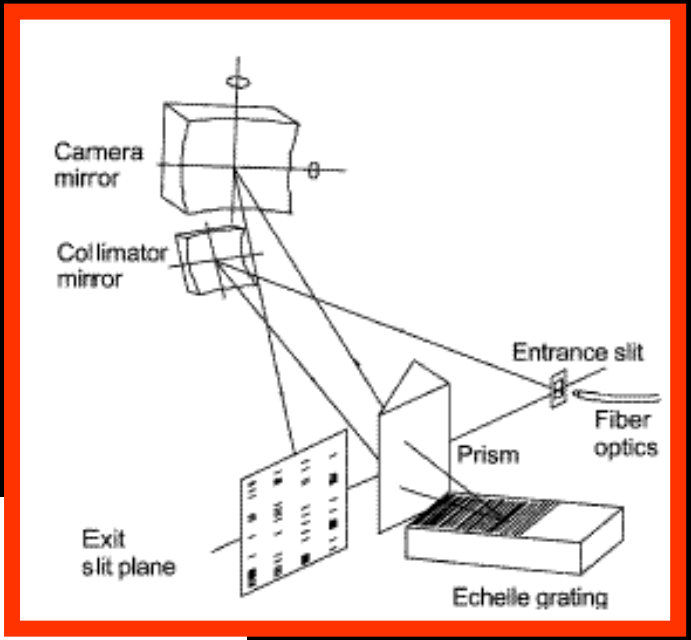
Specifications for the detection system

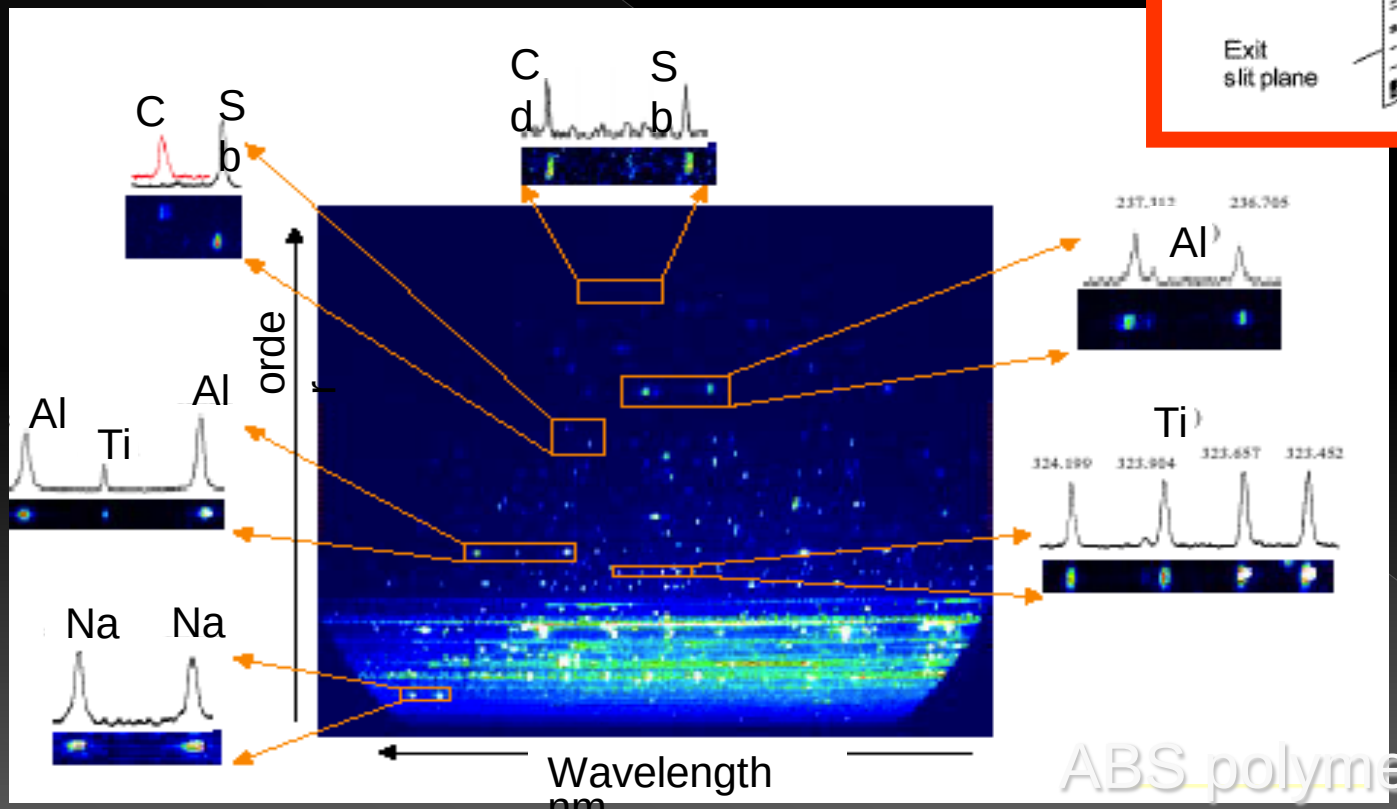


Spectral resolution: depends on the current analysis: matrix, elements. Resolution better than 0.1nm desirable

Echelle spectrometer

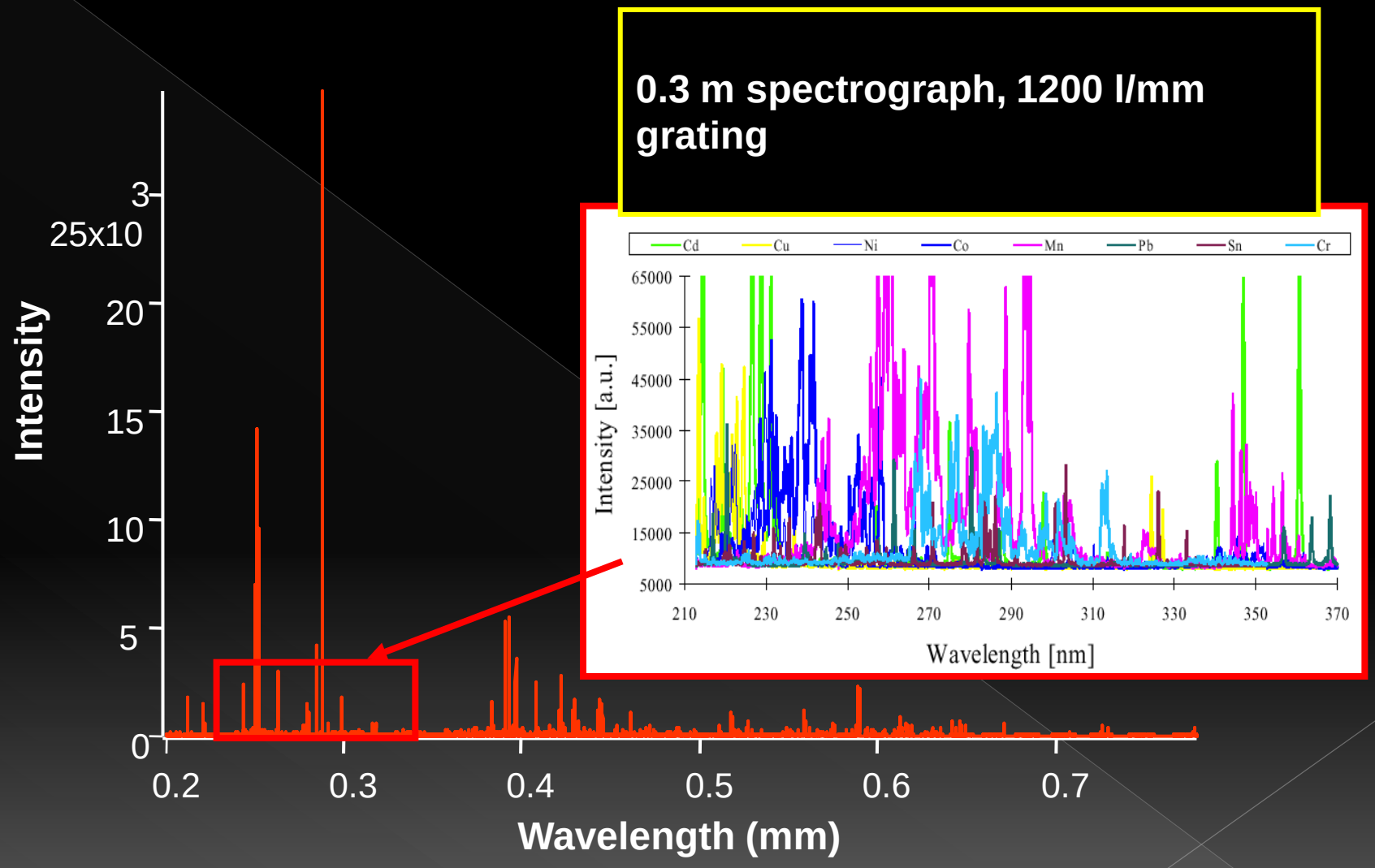
Spectral LIBS data on a 2D ICCD produced by an echelle spectrometer



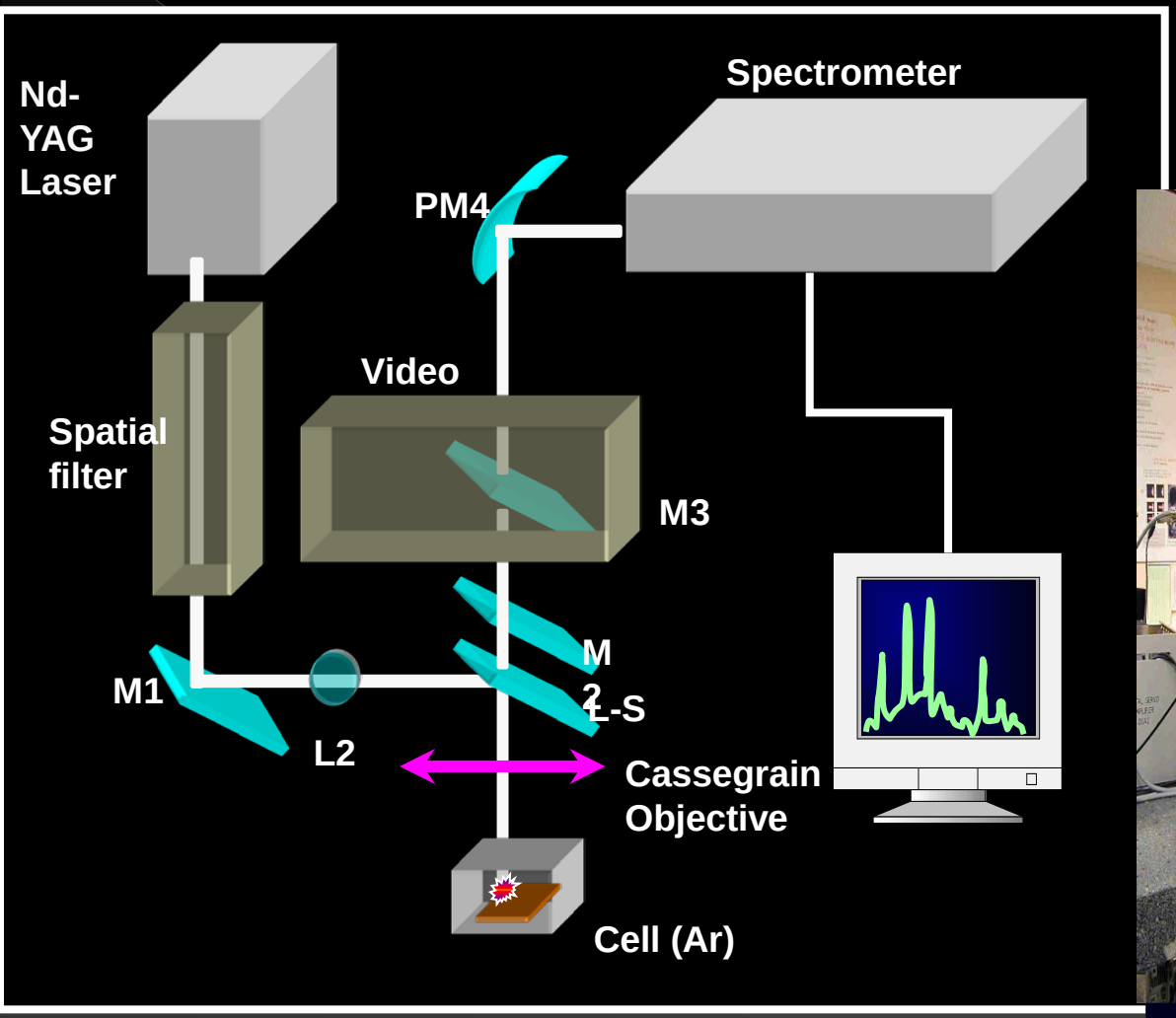


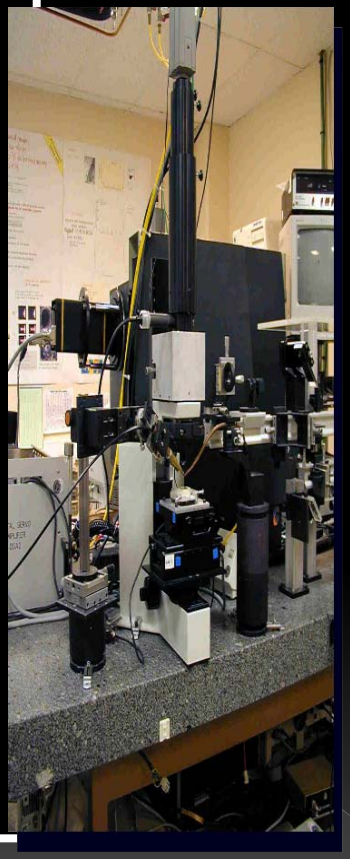
ABS polymer

Libs spectrum obtained with an echelle spectrometer



Micro-LIBS





Laboratory image

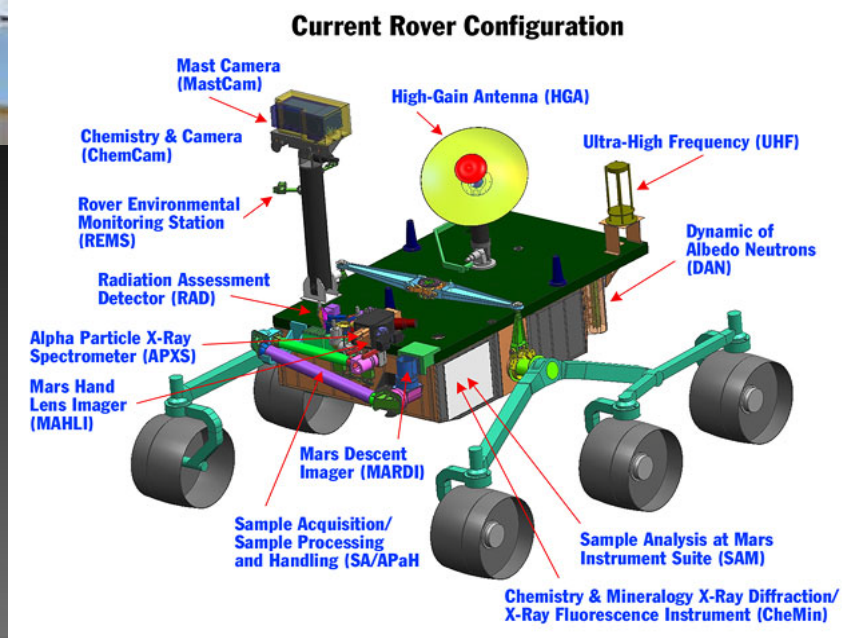
Micro LIBS at G2R- UMR 7566
Nancy Laboratory (France)

A LIBS for Mars

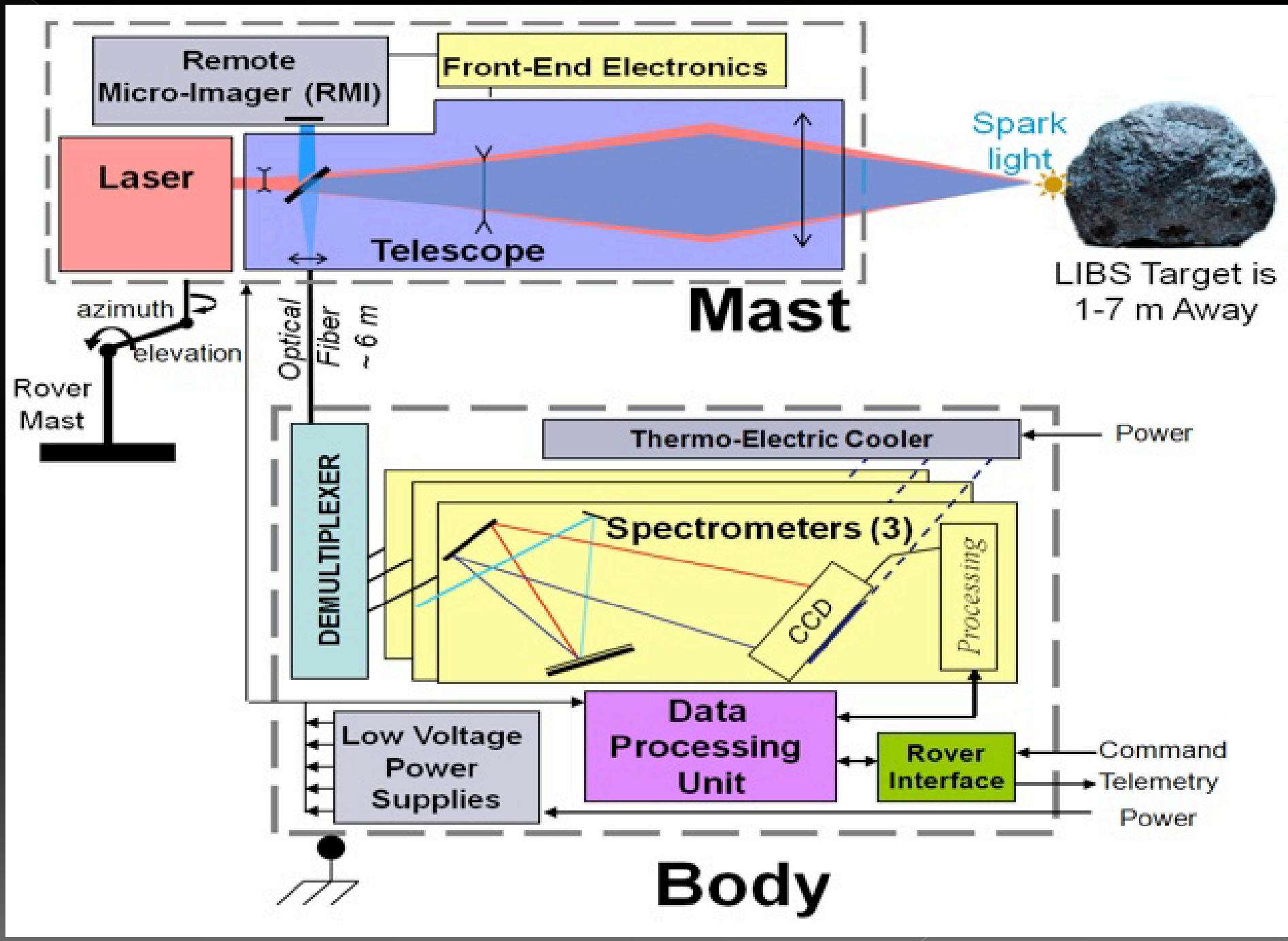
ChemCam

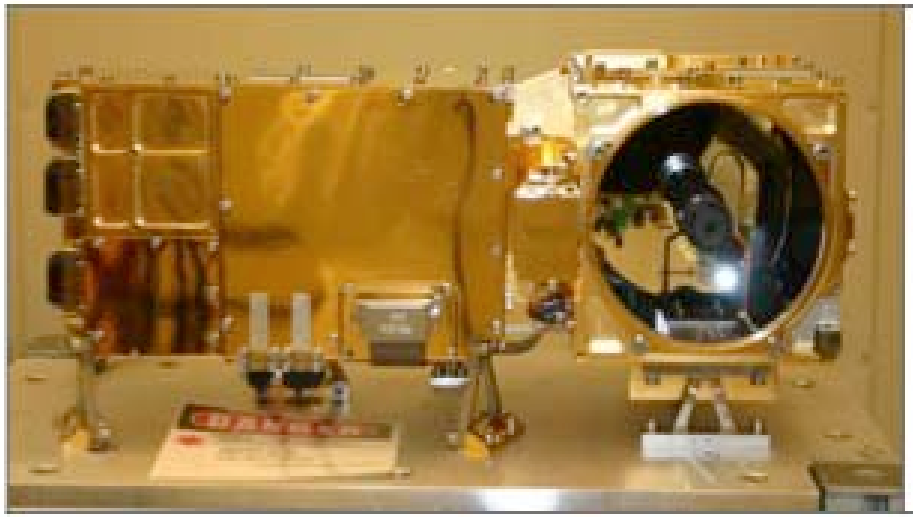
Laser-Induced Remote Sensing for Chemistry and Micro-Imaging

R. Wien (PI), S. Maurice (co-PI)

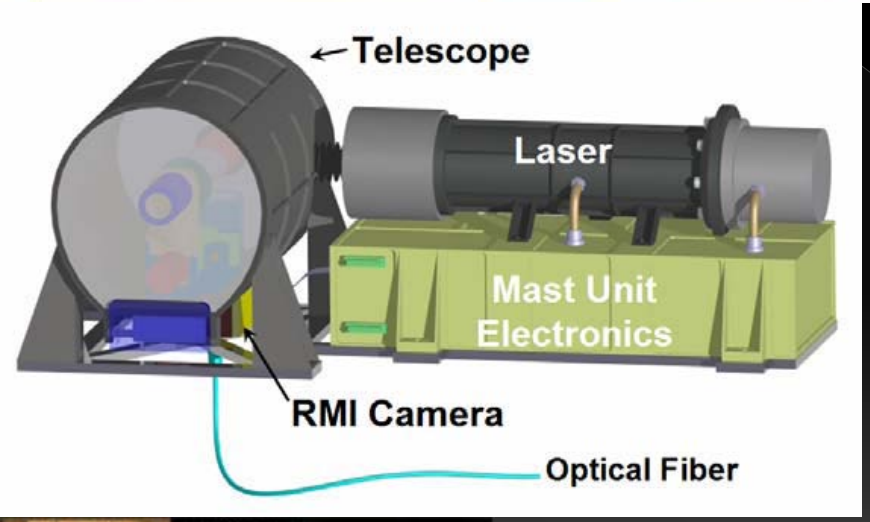


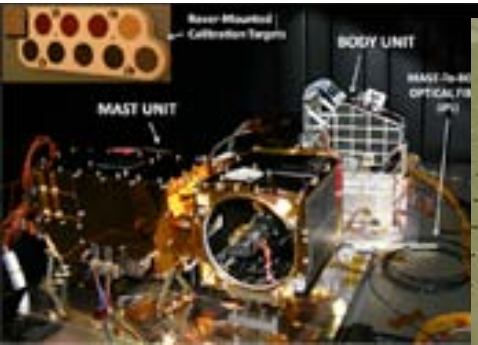
ChemCam in MSL rover

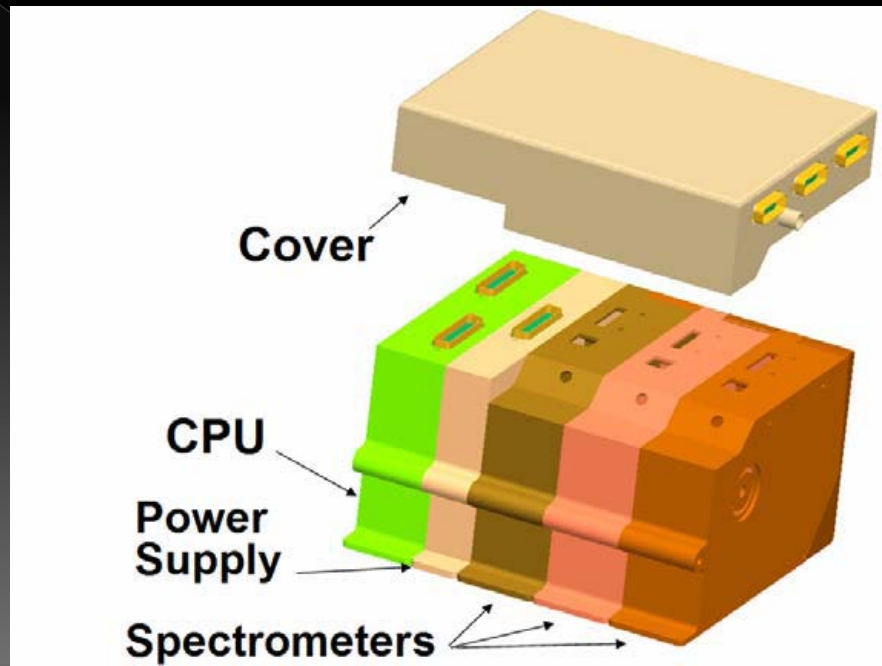

Remote
Micro-Imager (RMI)
Front-End Electronics
Laser
Telescope
Spark
light
LIBS Target is
1-7 m Away
Mast
azimuth
elevation
Rover
Mast
Optical
Fiber
~ 6 m
Thermo-Electric Cooler
Power
DEMULTIPLEXER
Spectrometers (3)
CCD
Processing
Data
Processing
Unit
Rover
Interface
Command
Telemetry
Low Voltage
Power
Supplies
Power
Body



Instrument main units



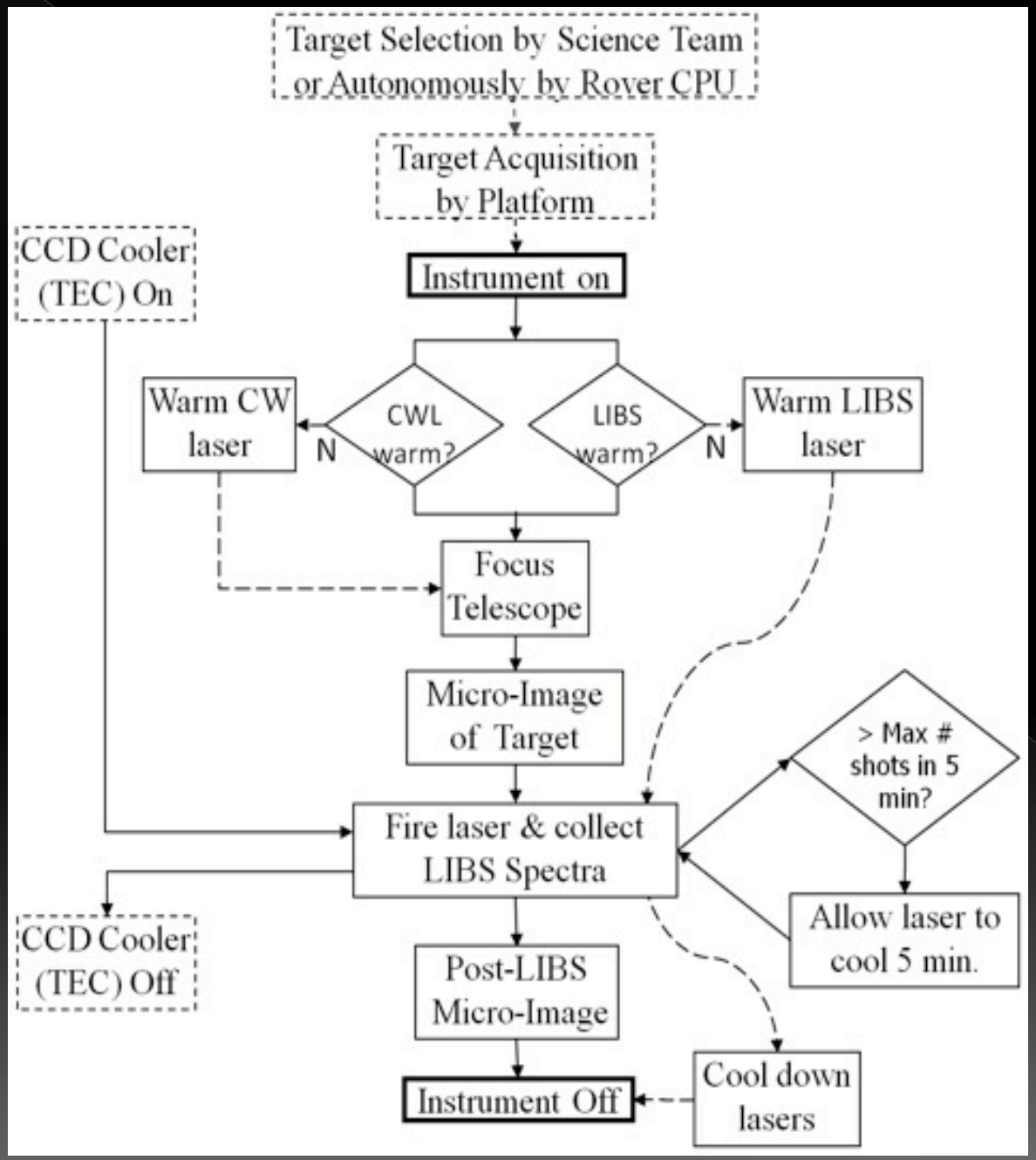




ChemCam technical characteristics

LIBS	
Range	2-13 m
Depth Profile Rate (basalt & sand)	~0.4 μm/pulse ~0.1 mm/pulse
Analysis Spot	0.5-1 mm dia
Laser	
Power	30 mJ/pulse
Wavelength	1067 nm
Pulse Rate	15 Hz
Pulses per Burst	75
Recharge Rate	40 sec/burst
Spectrographs (3)	
Design	Czerny Turner
Range	240-800 nm
Resolution	0.09-0.3 nm
CCDs, # pixels	Linear, 2048
Signal/Noise	250

RMI	
Optics design	Schmidt
Aperture	100 mm dia
Range	2 m – infinity
Spatial resolution	80 μrad
Wavelength range	800-1000 nm
Exposure range nominal	2 ms – 8 s 75 ms
MTF at Nyquist	0.10 – 0.44
Overall	
Mass	5.62 kg (+cable)
Volume	8904 cc
Power (6.7 W ave)	3.9 W-hr/sol
Data Volume	12.0 Mb/sol



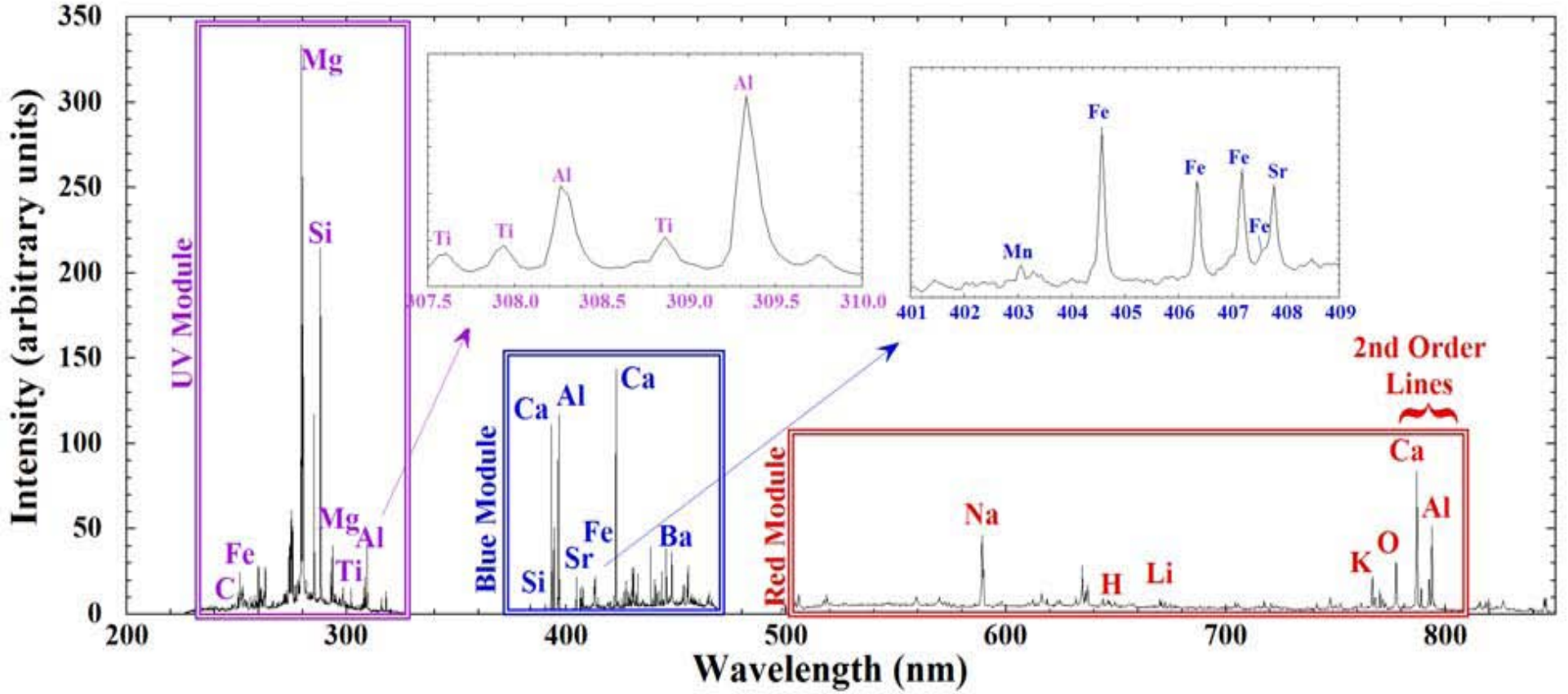
ChemCam scientific operation cycle

The telescope is focused on the target. RMI image acquisition and LIBS analyses are performed, and a background (laser-off) spectrum is taken.

The mast can then acquire other targets and the focus and shoot sequence can be repeated.

Calibration targets

LIBS results: identification and quantification



LIBS soil spectrum recorded at a distance of 5.3 m shows fifteen elements ranging in abundance down to a few ppm. The three modules correspond to the ChemCam spectrographs.

R.C. Wiens, ChemCam, FactShet

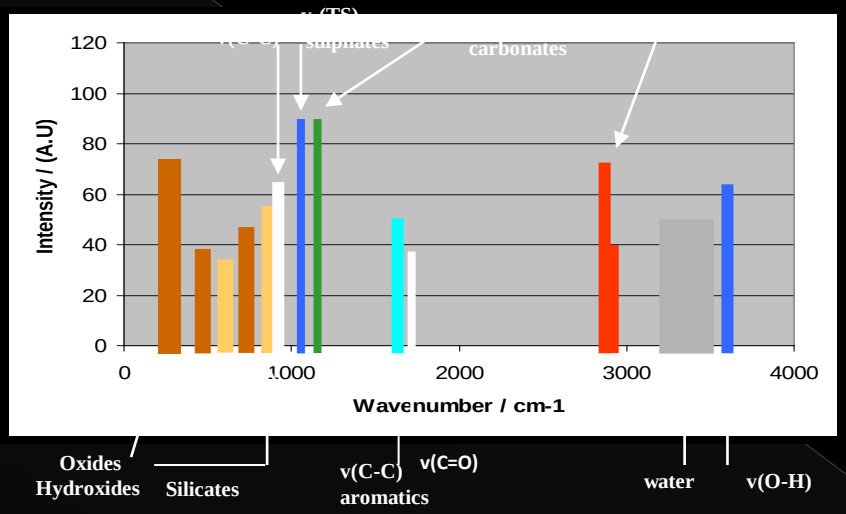
The combined Raman-LIBS

The precise characterization of materials at the atomic-molecular level is based on the structure-composition information .

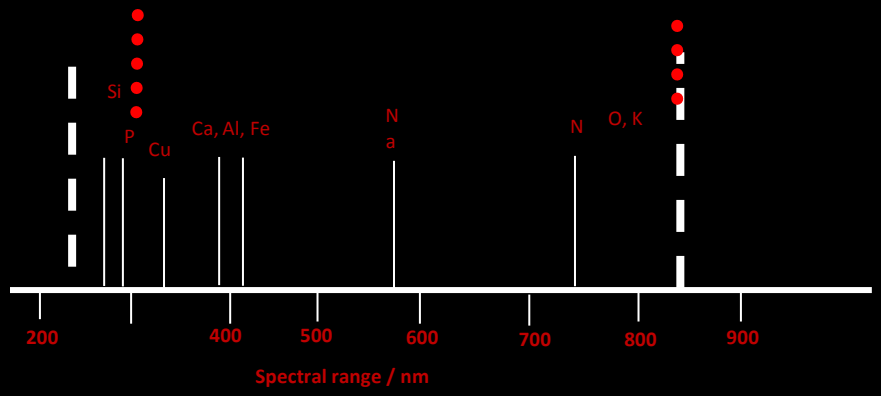
In consequence any technique combining these two capabilities in a single instrument is a very powerful technique.

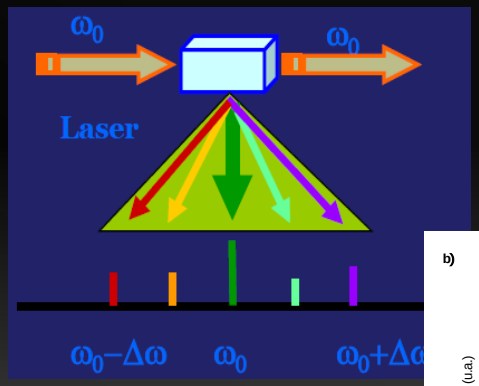
Raman-LIBS is one real possibility and in remote mode near the “perfect” technique for fast and reliable characterization of materials

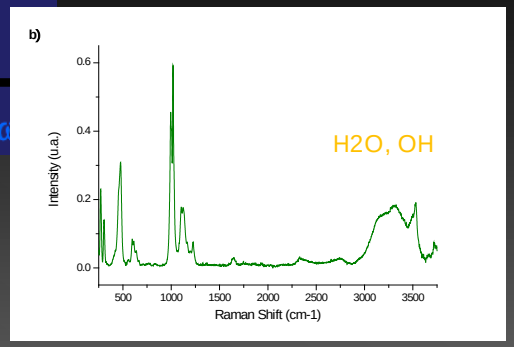
Raman Detection Capability

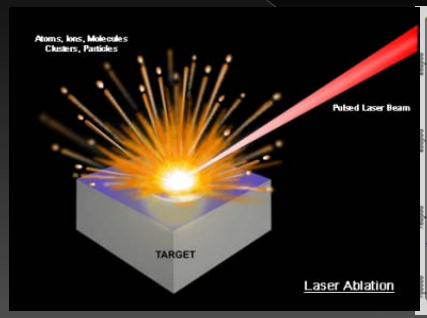


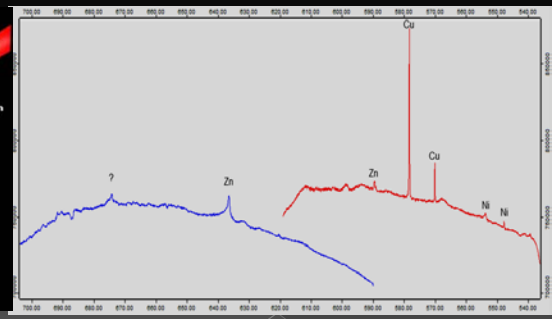
LIBS Detection Capability



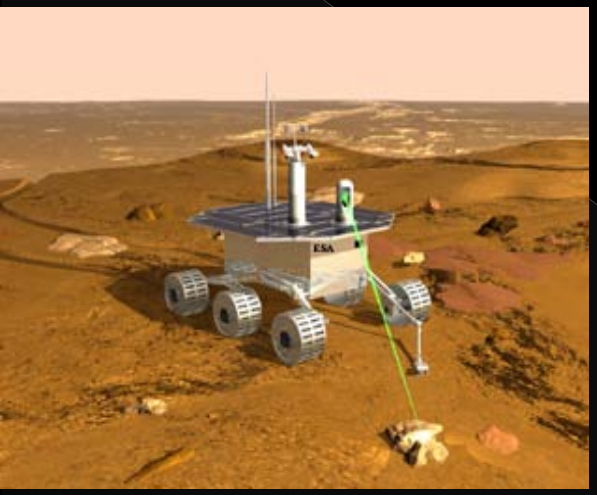


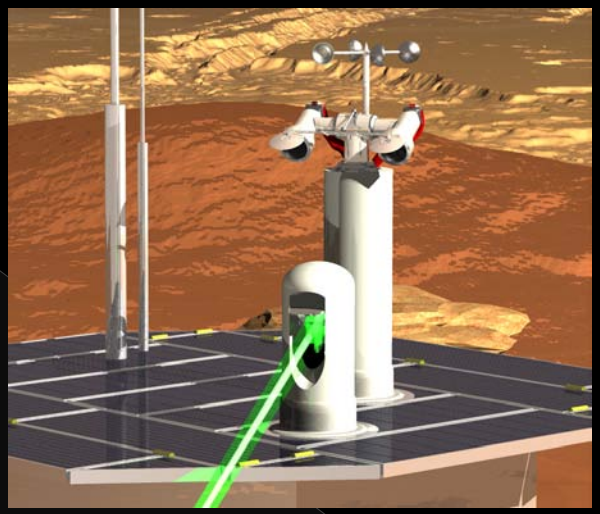




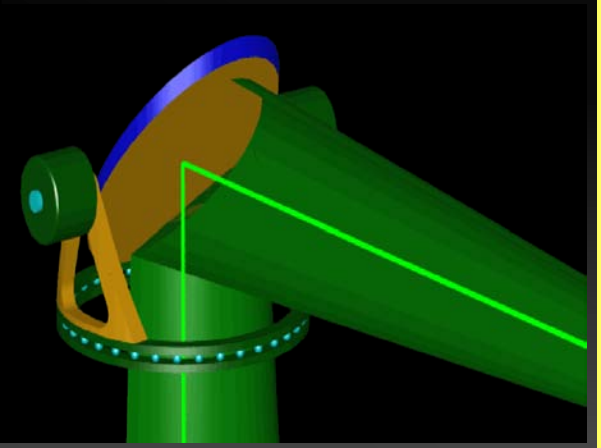


EXLIBRIS project for ExoMars (S. Maurice, F. Rull)





Proposal 2003

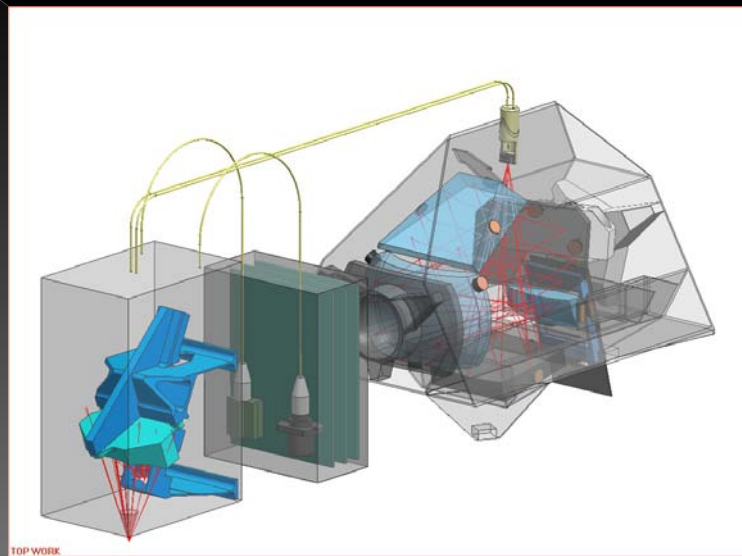


Implement <u>simultaneously</u> LIBS and Raman to study: **Chemistry**

Mineralogy

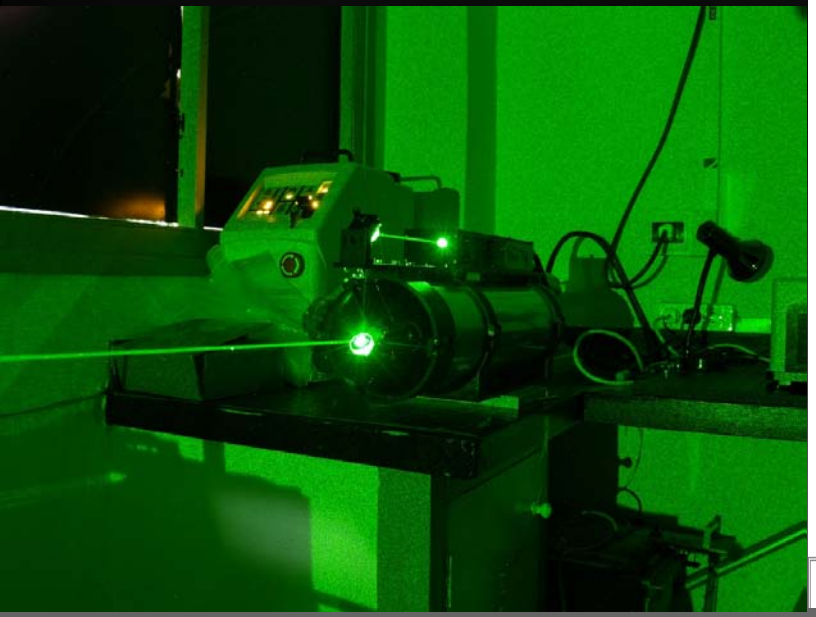
Organics

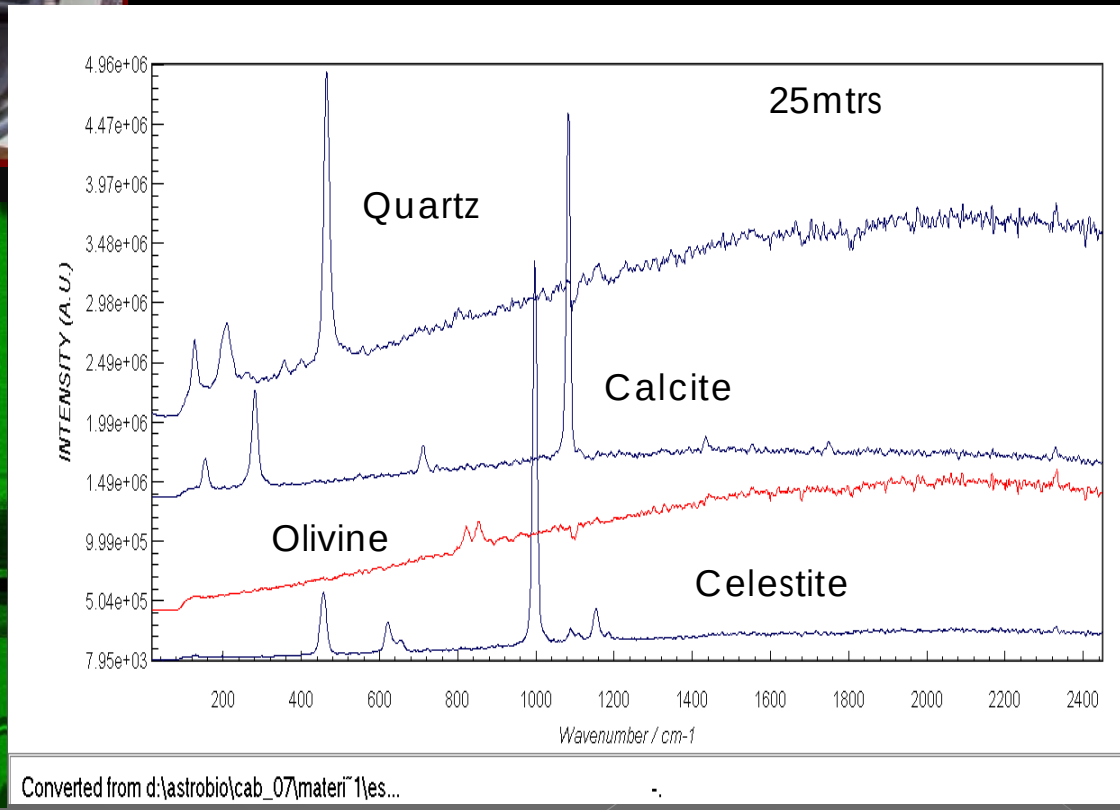
Raman-LIBS EBB (2007)
TNO Science and Industry



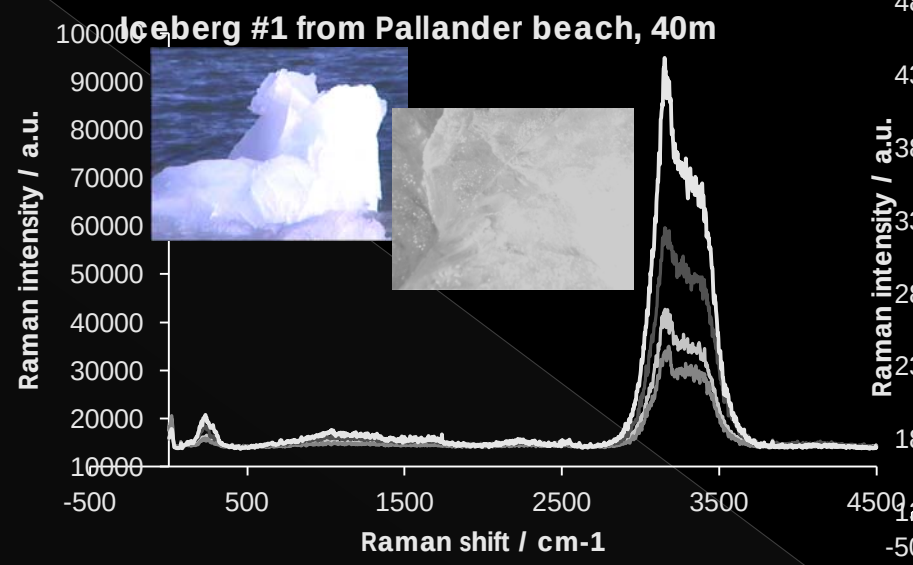
Remote Raman

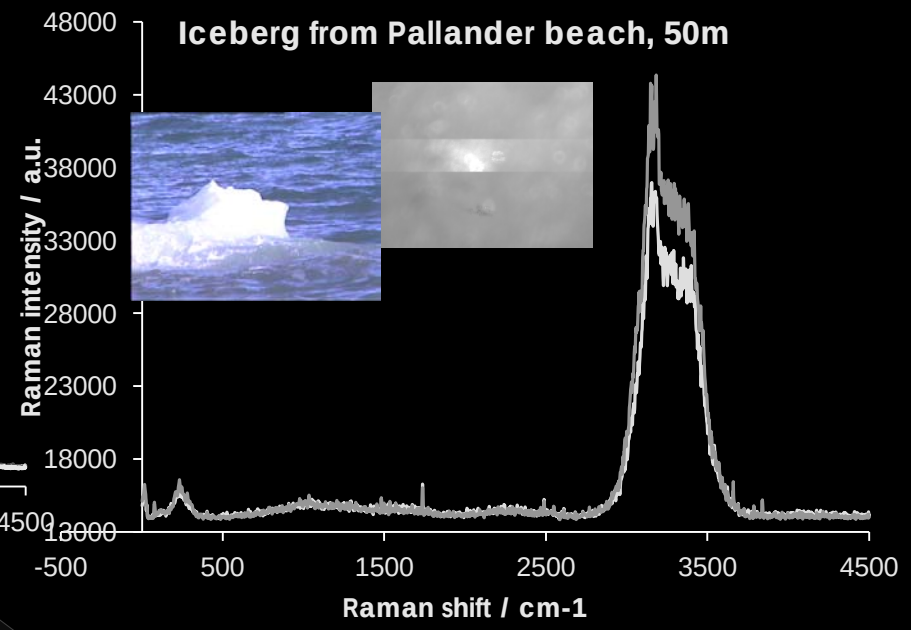
At UVA-CAB

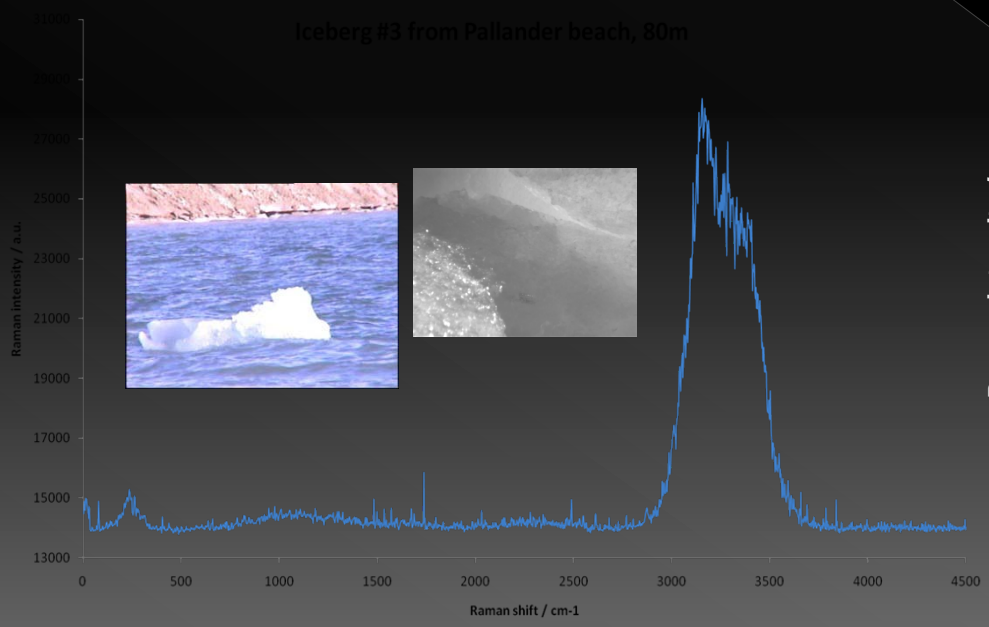


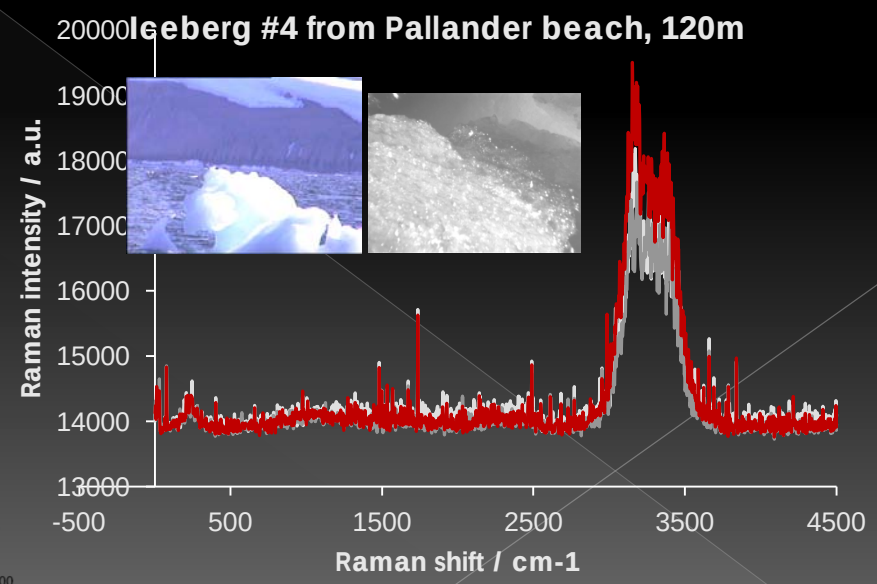


AMASE 2008


Iceberg #1 from Pallander beach, 40m
Raman intensity / a.u.
Raman shift / cm-1
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
-500
500
1500
2500
3500
4500

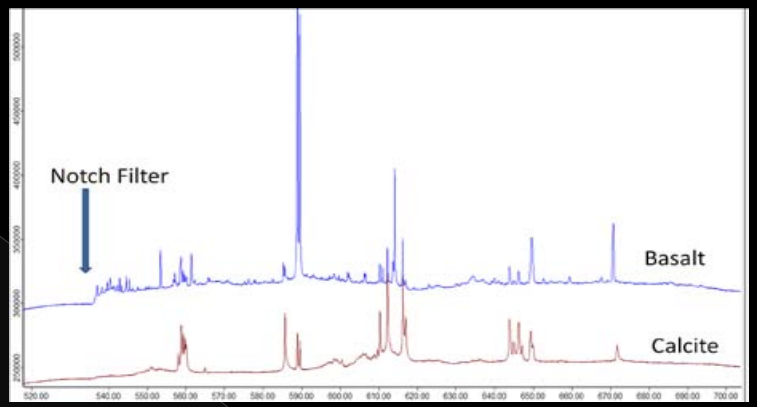

Iceberg from Pallander beach, 50m
Raman intensity / a.u.
Raman shift / cm-1
48000
43000
38000
33000
28000
23000
18000
13000
-500
500
1500
2500
3500
4500

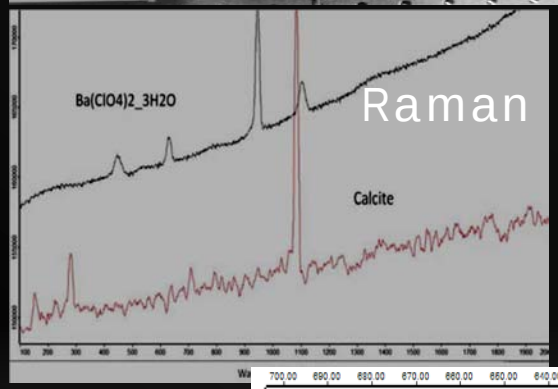

Iceberg #3 from Pallander beach, 80m
Raman intensity / a.u.
Raman shift / cm-1
31000
29000
27000
25000
23000
21000
19000
17000
15000
13000
0
500
1000
1500
2000
2500
3000
3500
4000
4500


Iceberg #4 from Pallander beach, 120m
Raman intensity / a.u.
Raman shift / cm-1
20000
19000
18000
17000
16000
15000
14000
13000
-500
500
1500
2500
3500
4500

Combinación Raman-LIBS (15 mtrs)

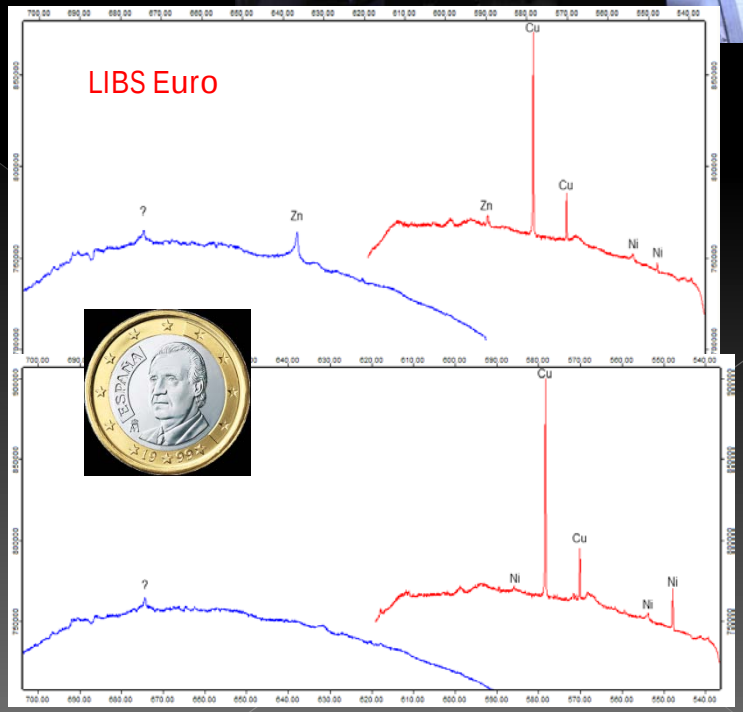
LIBS



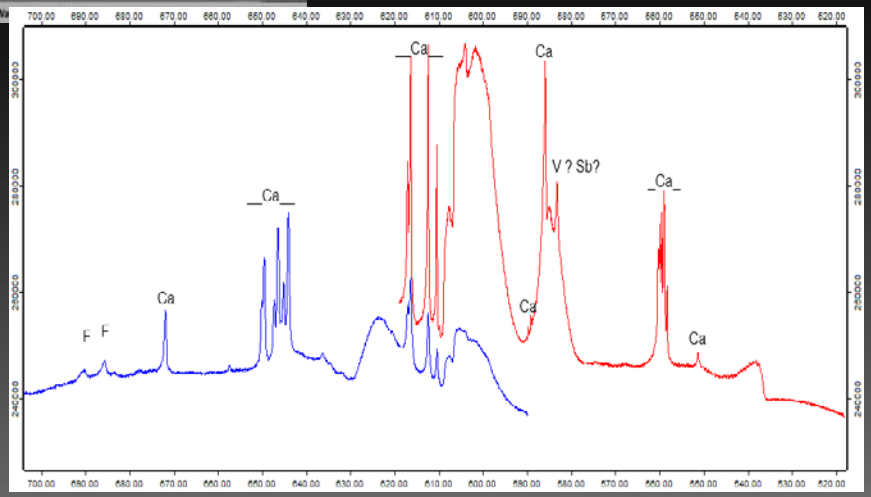


Raman

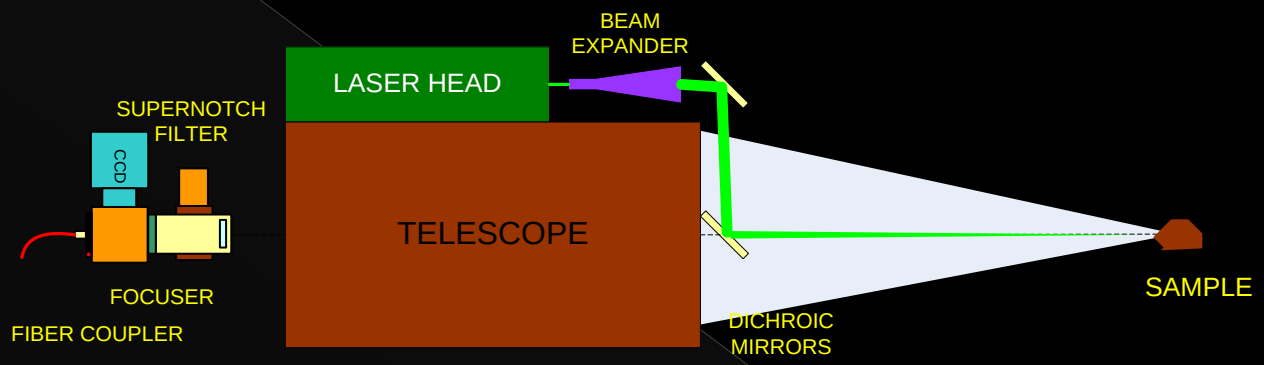
LIBS Euro

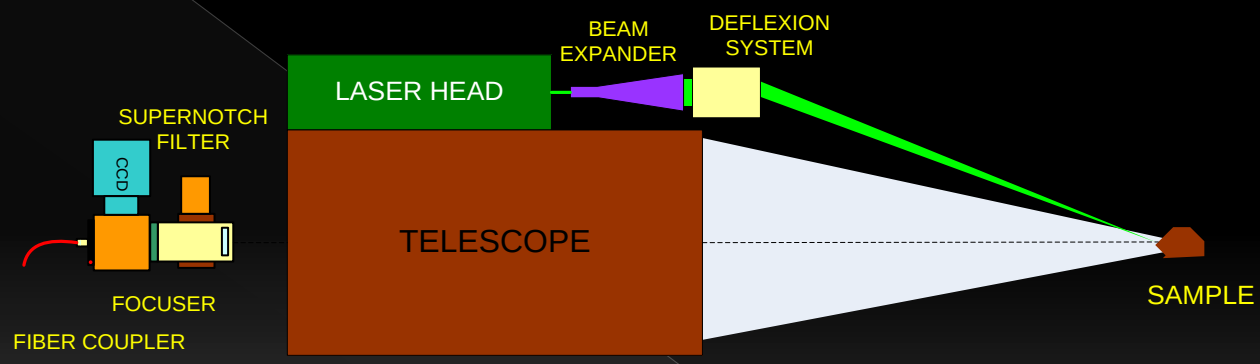


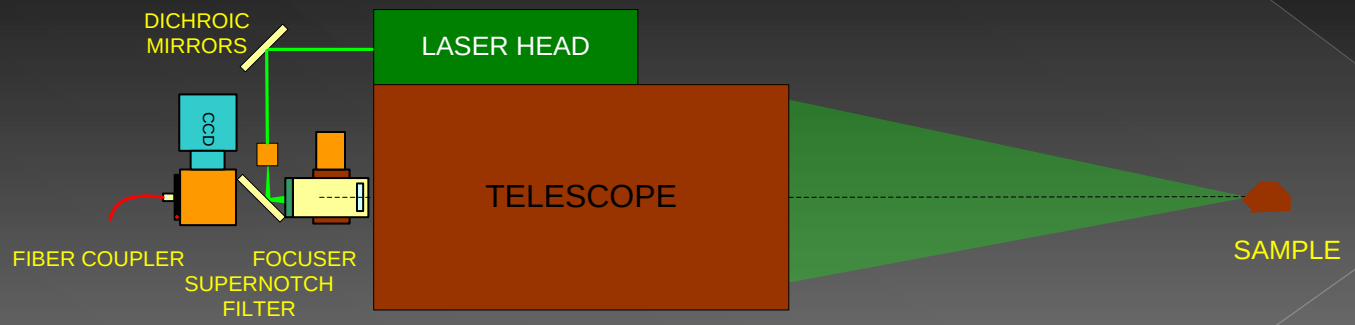
LIBS
Fluorita

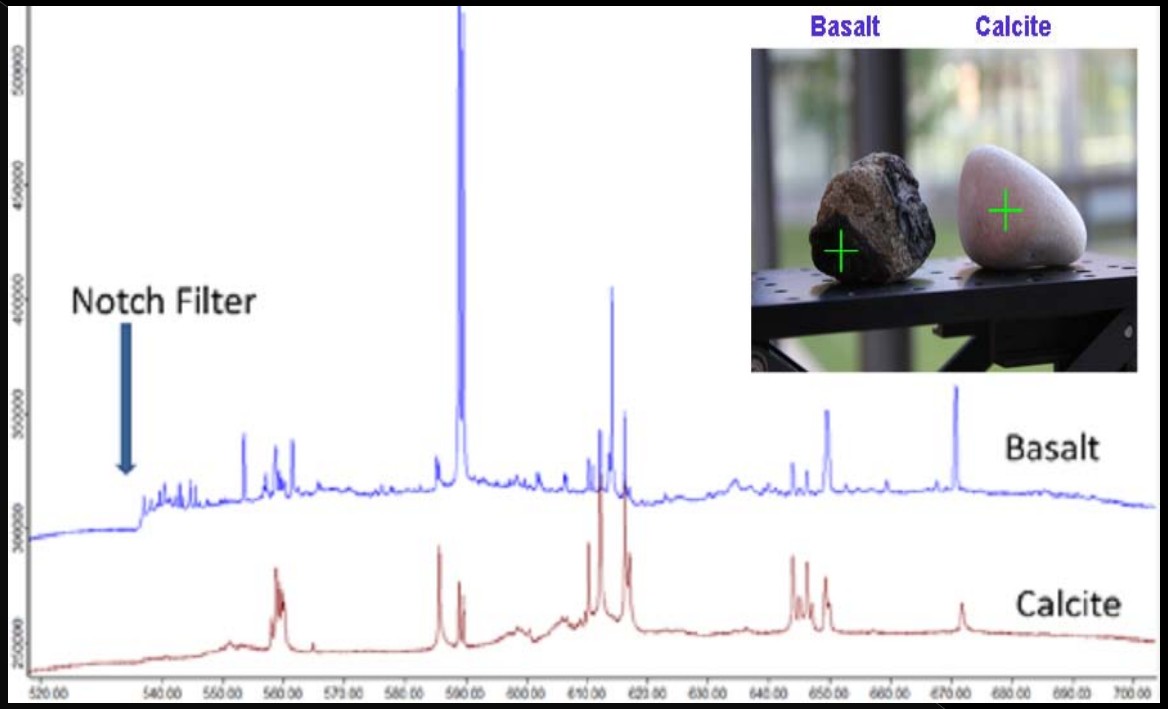


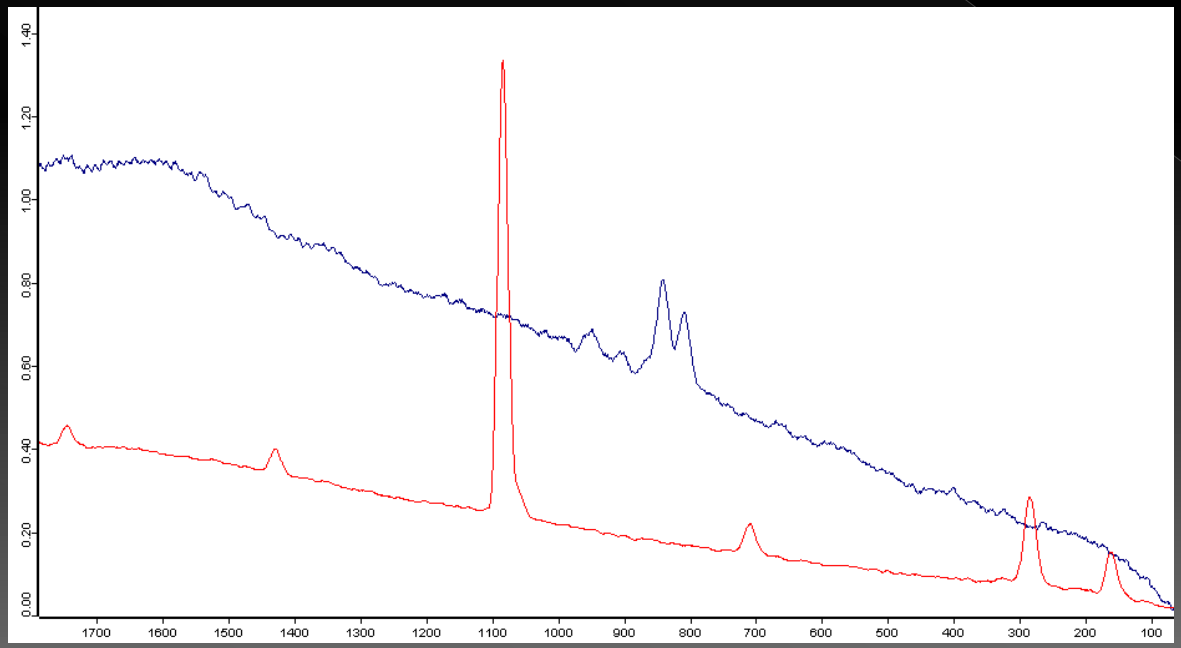
Optical configurations











Gated vs. Non gated

LIBS and Raman spectra of calcite and basalt at 6 meters distance obtained with the non gated CCD.

Partially cloudy conditions.

Conclusions

Raman and Libs give very precise information on the structure and elemental composition of the materials respectively.

When operating at the same time and on the same spot this information is extremely useful

And when operated in remote mode this microscopic information can be obtained from wide areas in a fast time contributing strongly to establish the "context science" and to the rapid evaluation of the samples.
This is of great value for robotic exploration of the surface and for selecting appropriate samples (return missions)

Thanks for your attention