LIBS applications and industrial aspects

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DE LA RECHERCHE À L'INDUSTRIE

cea den

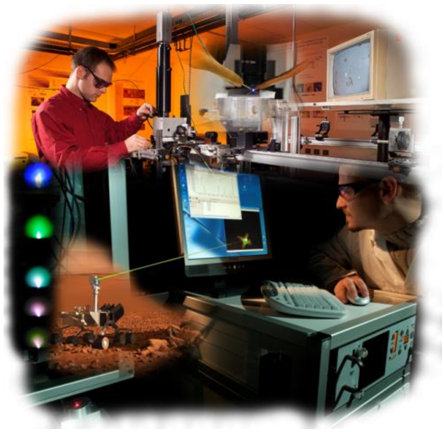
20A ESCUELA OPTOANDINA QUITO-2015

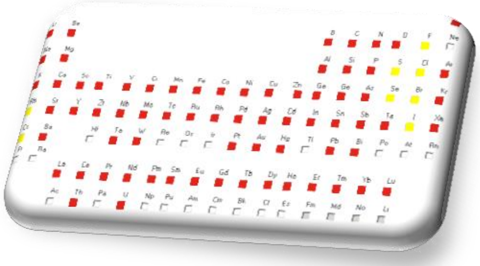
LIBS APPLICATIONS AND INDUSTRIAL ASPECTS

Daniel L'HERMITE

CEA / DEN / DPC / SEARS / LANIE

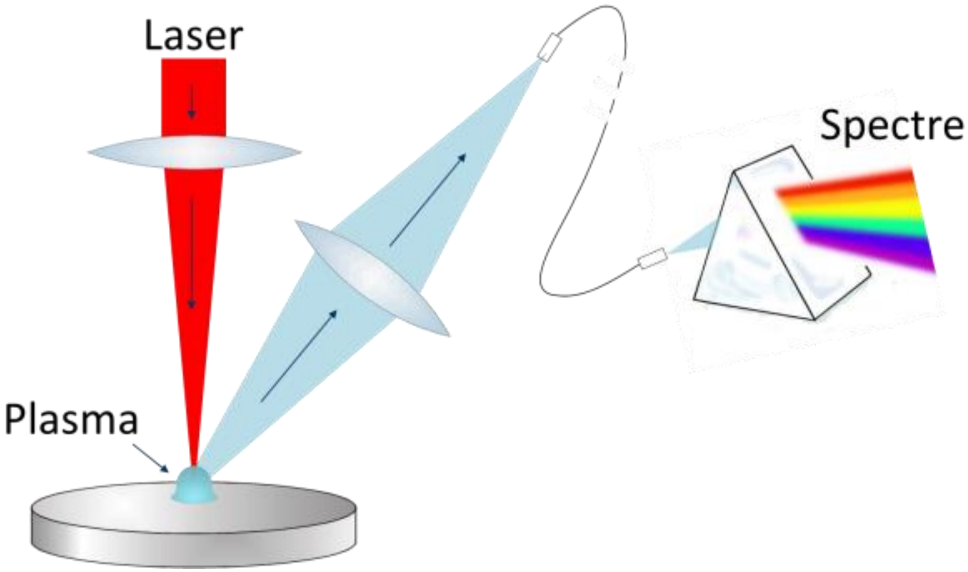
CEA Saclay





OPTOANDINA 2015, 9-13 Nov. Quito, Ecuador

LIBS PRINCIPLE



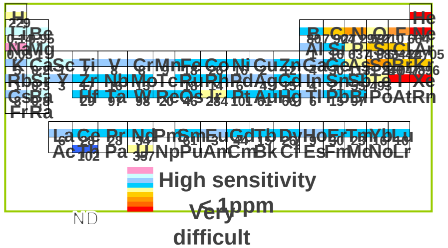
- ❑ **Measurement on all kind of materials**

Solid liquid gas aerosols

- ❑ **No sample preparation**

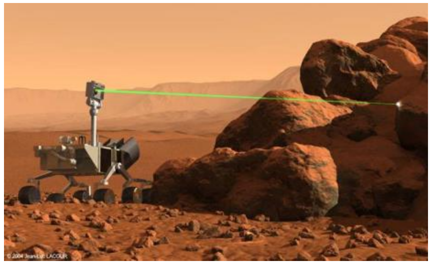
R.Bruder CEA and LRMH

- ❑ **Multi-elementary measurement**



- ❑ **Remote measurement**

Like "Curiosity" Landing on Mars on August 2012



- ❑ **Real-time measurement (1sec to a few min)**

LIBS is well adapted for in-situ and field analysis

INDUSTRIALISATION

Industrialization means :

- ❑ Robustness → No change in the measurement during time and limited changes vs external conditions (temperature, humidity, chocs, dust,…)

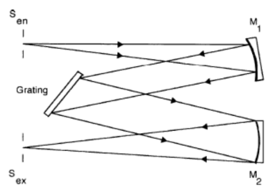
- ❑ System control → Repeatability, reproducibility, and quickly

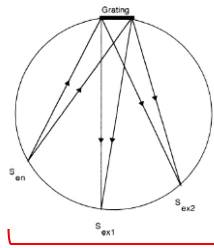
- ❑ Data treatment → For non expert users

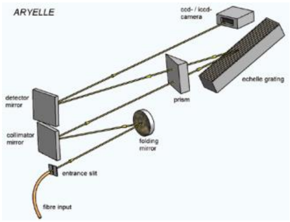
ROBUSTNESS : DEVICES

Spectrometer

Monocromador *Policromador* *Echelle* *Compacto*







Moving part (grid)

No moving part

All are sensitive to the temperature → thermalization

Laser (Nd:YAG in general)

Pump by

- Flash lamp → not expensive but energy decrease and the lifetime is not too long (1 month 24/24)
- Laser diode → Expensive but stable and long lifetime

λ

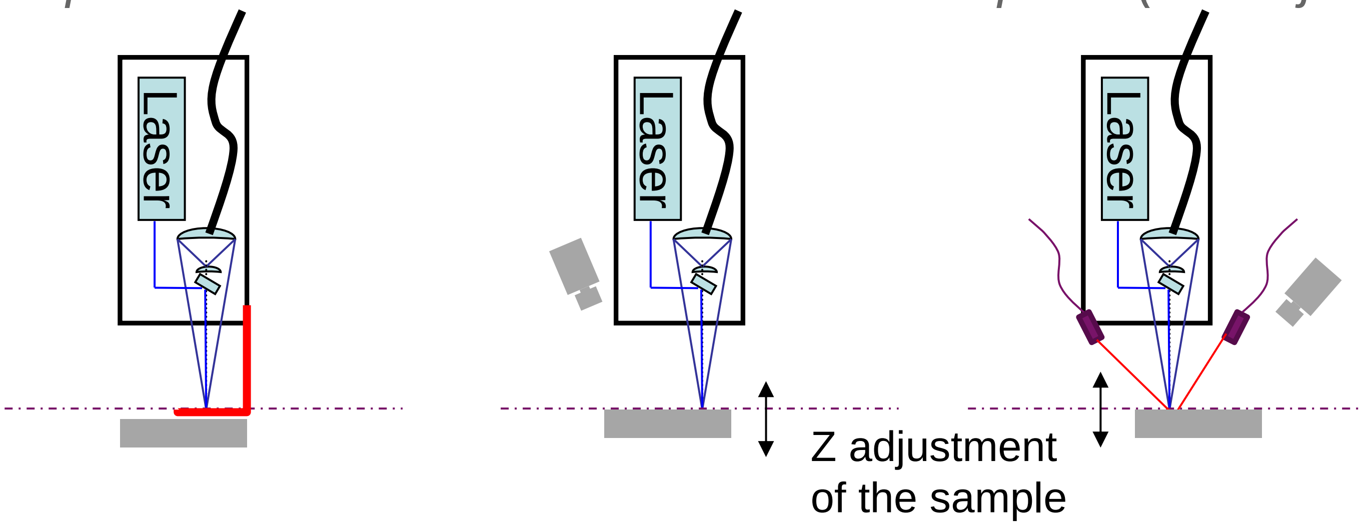
- 1064nm : no harmonic crystal
- 532nm : 1 crystal
- 355 and 266nm : 2 crystals

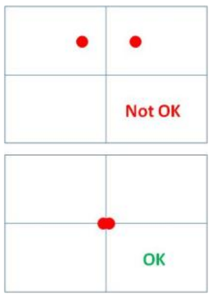
Pb of stability with temperature and mechanically

SYSTEM CONTROL

What kind of “options” does a industrial LIBS system should have?

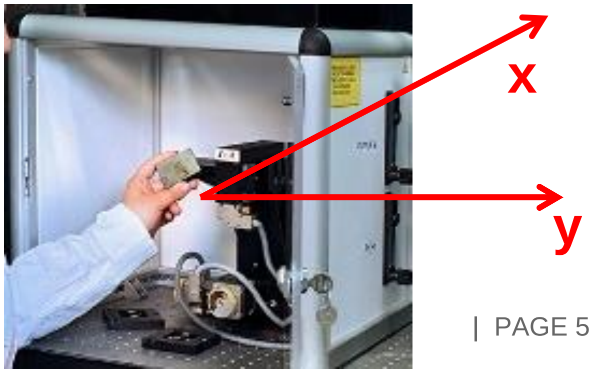
- ❑*Lens/sample distance control → mechanical or optical (+ z adjustment)*





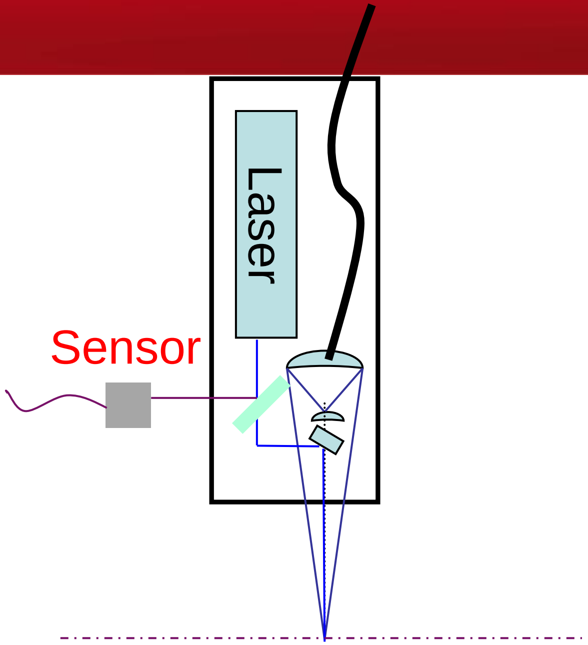
- ❑*Duplicate measurements for statistical purpose (typically > 20) → x,y motors*

Goal : to acculate many laser shots (best S/N ratio), to have a good estimation of the mean signal <S> and to have an idea of the repeatability with the standard deviation σ_S

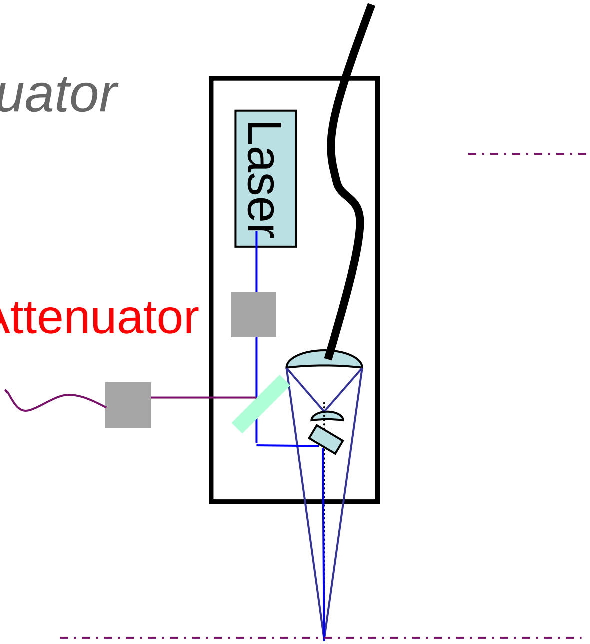


SYSTEM CONTROL

- *E_{laser} measurement (for normalization) : in order to perform quantitative analysis*

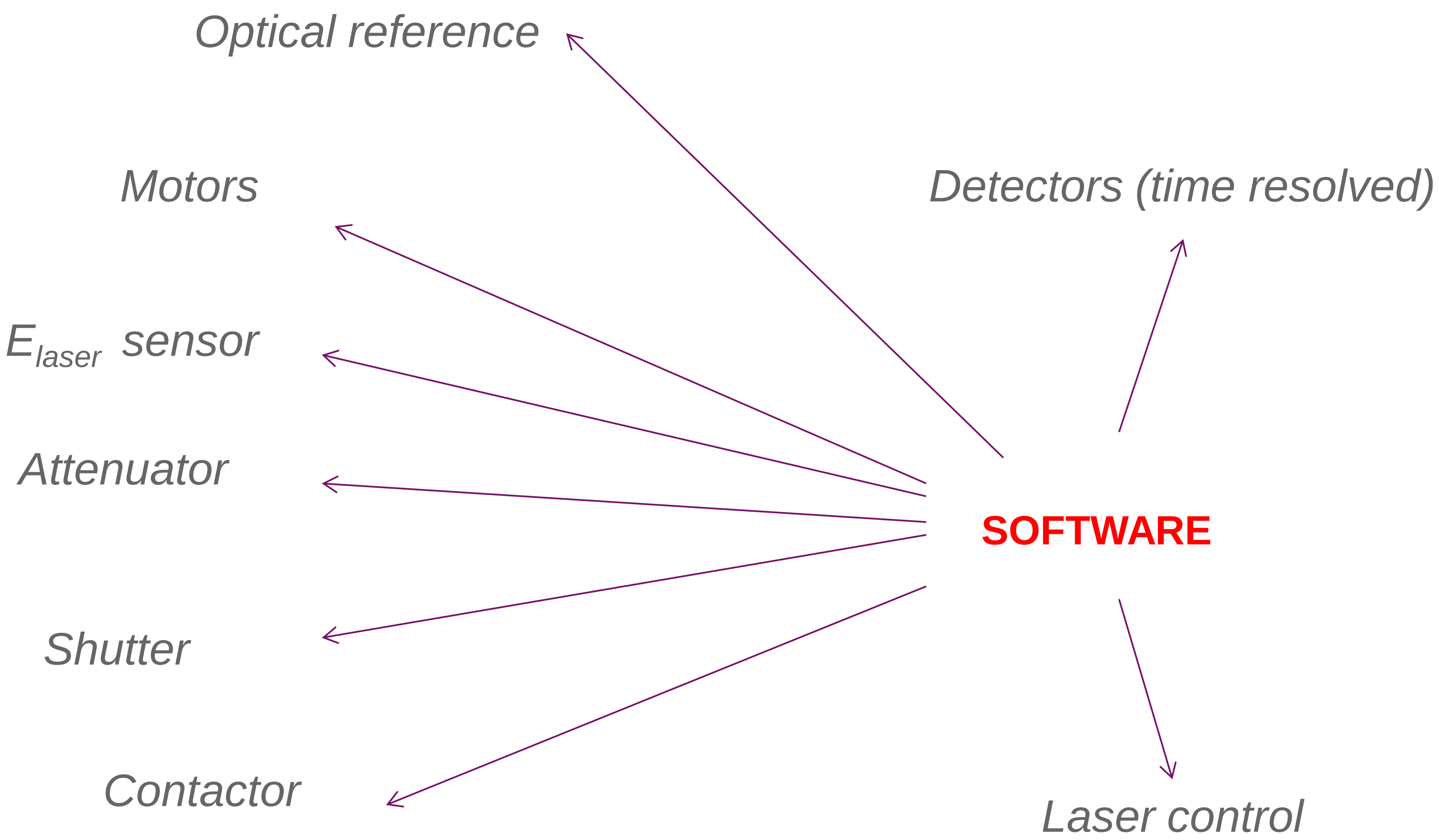


- *E_{laser} adjustment → optical attenuator*



- *Shutter to have a stable laser*
- *Contactor for laser safety*

SYSTEM CONTROL = DEVICES CONTROL



→ Could be complex (pb of timing, synchronization)

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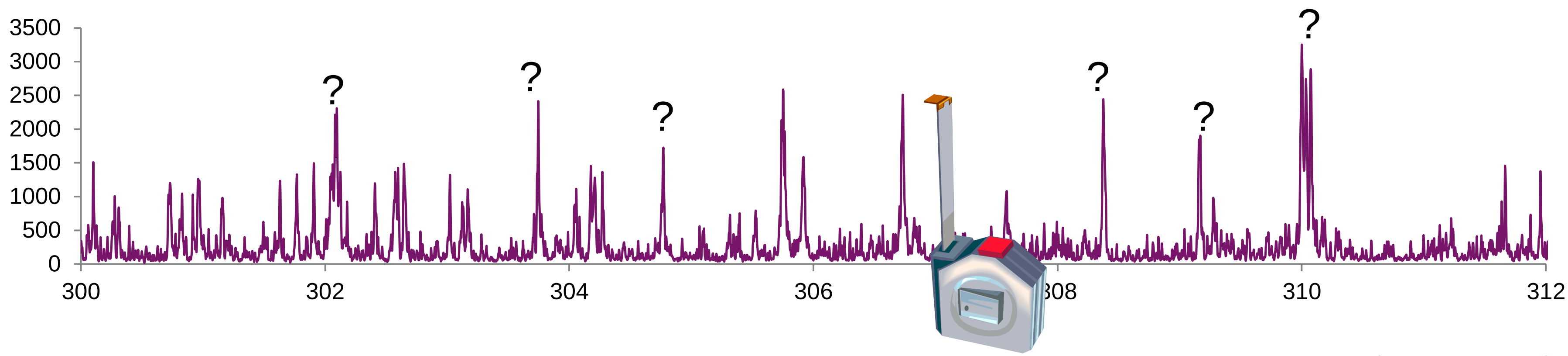
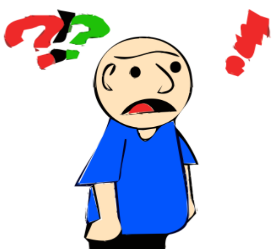
DATA TREATMENT



A user who buy a LIBS system is not a specialist of LIBS



→ The manufacturer may adapt its LIBS software to the final needs

→ The result must be friendly to use

Cr 19,2%

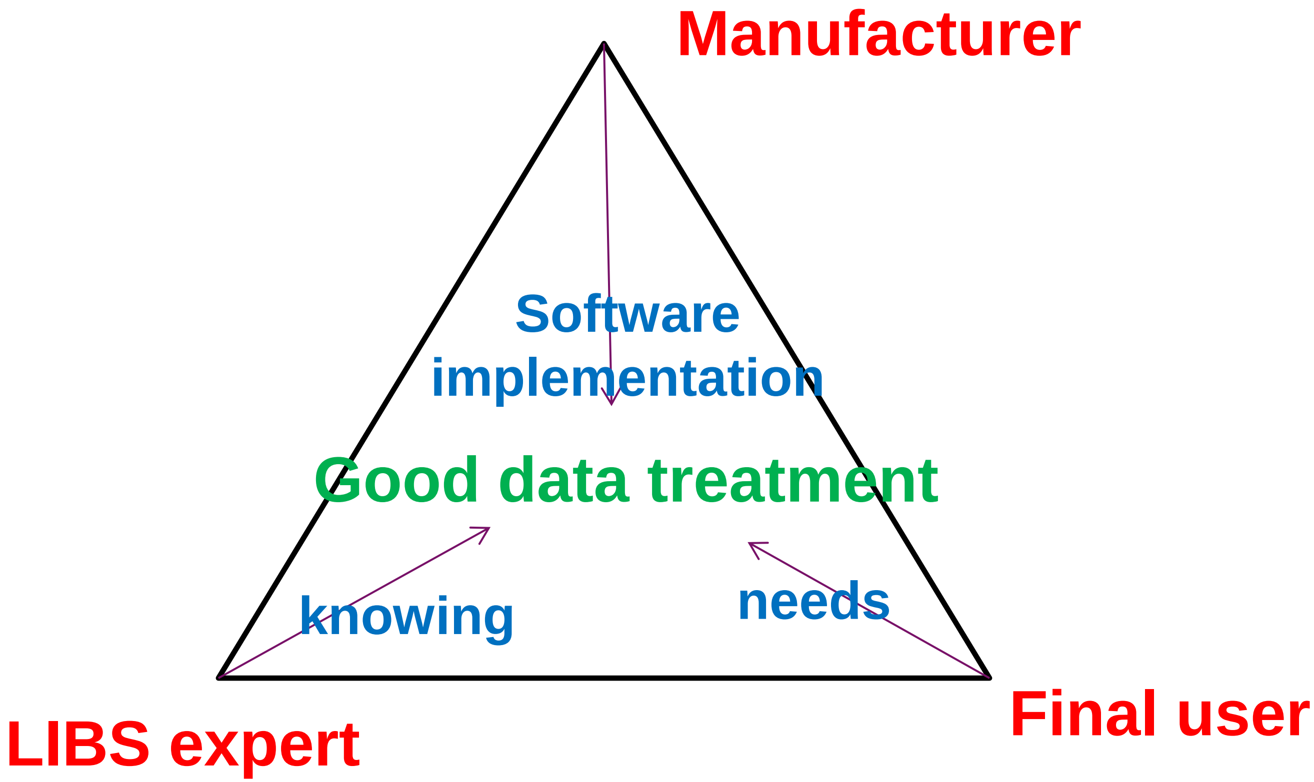
Bronze

good | Not good

DATA TREATMENT (2)

To have a succesfull data treatement,

I suggest this association



TO RESUME

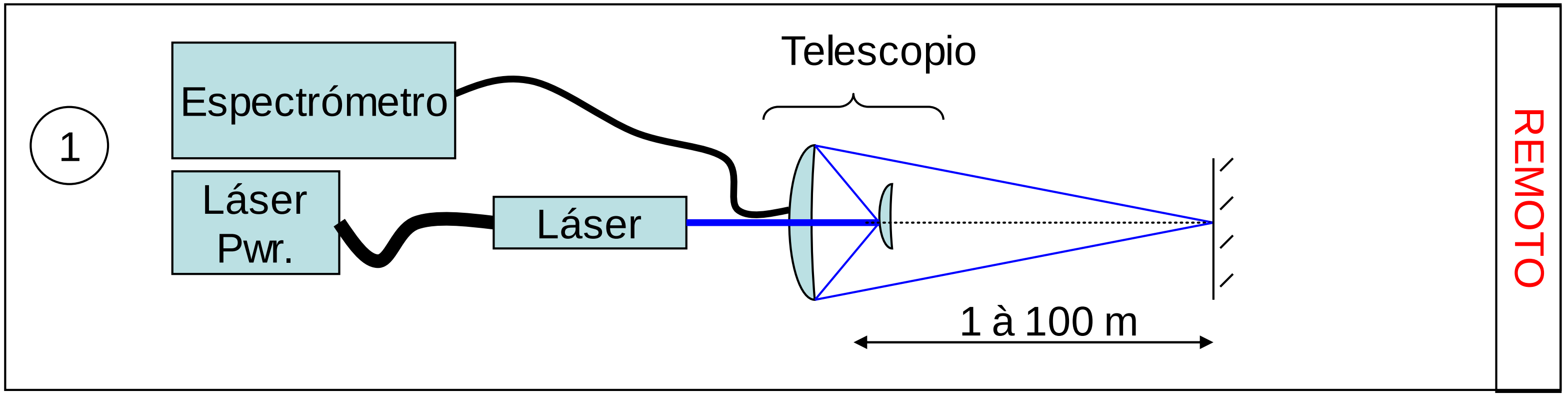
The manufacturer have many things to implement and to manage (devices) and
Data treatment have to be adapted for each “user”

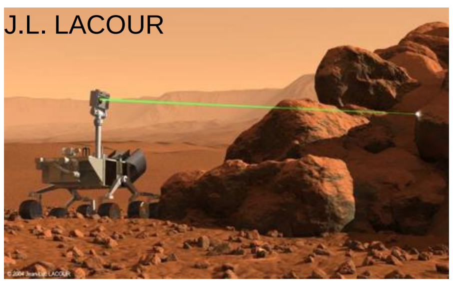
- **Cost ↗ and the market are actually not so big (niche market)**
- **Actually the volume of the market are not enough to obtain a decrease of the prices (laser and spectrometer).**

Hard work but actually many manufacturers propose different LIBS systems

Examples of industrial systems

STAND-OFF CONFIGURATION





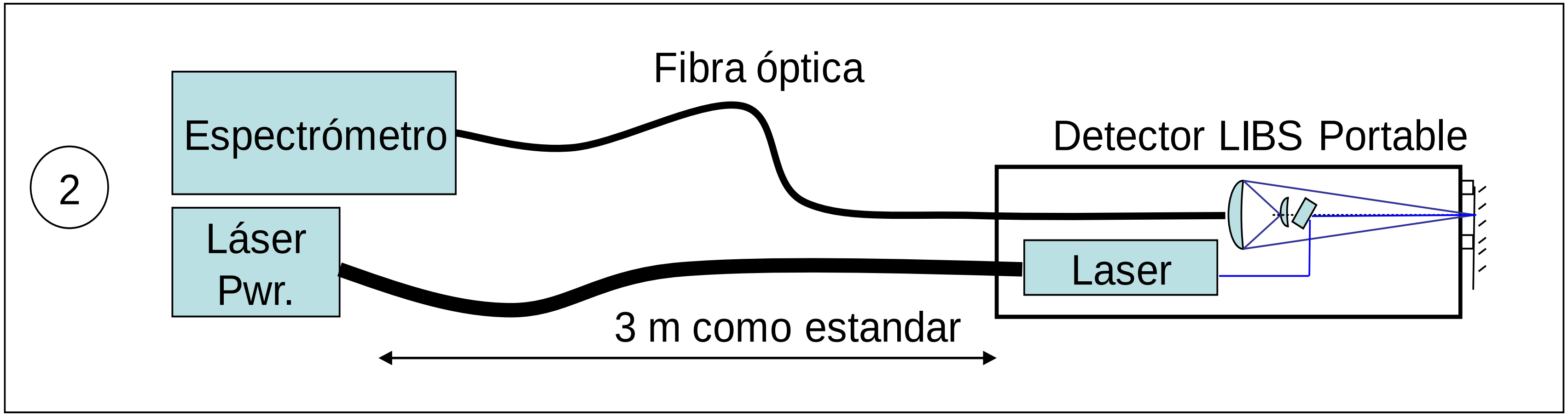
Chemcam,
NASA(usa), CNES (fr)

FARLIBS, IVEA (fr)

Applied photonics (uk)

TeleLIBS, LSA (de)

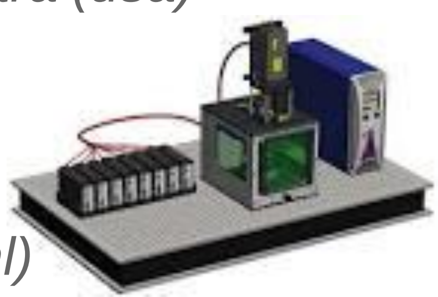
BENCH TOP CONFIGURATION



MOBILIBS, IVEA (fr)

LIBSLab, LTB (de)

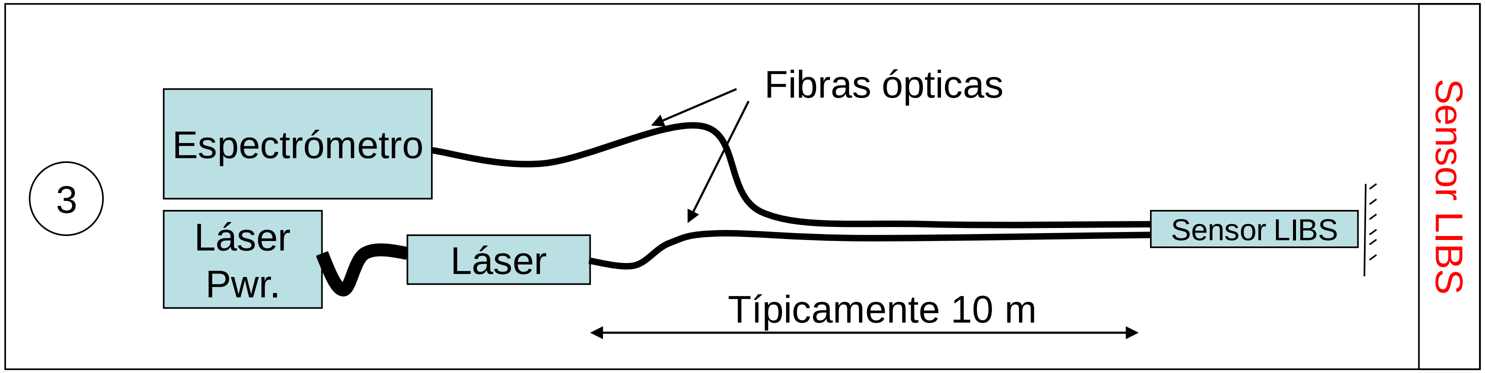
Applied spectra (usa)



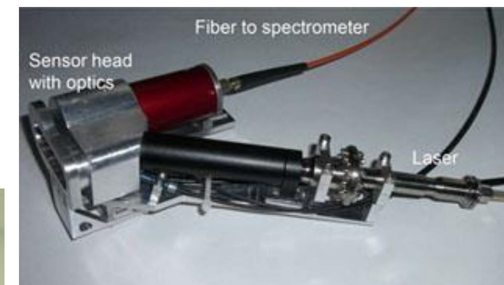
Avantes (nl)

LIBSscan, Applied photonics (de)

REMOTE (FIBER) CONFIGURATION



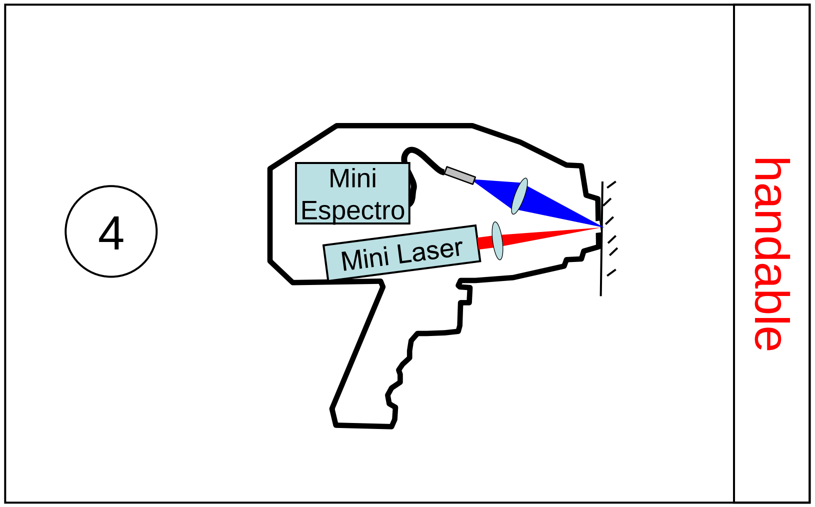
OFILIBS, IVEA (fr)



DLR,(de)

Applied photonics (uk)

HANDABLE CONFIGURATION



EASYLIBS
IVEA (fr)

Katana
Rigaku (jp)

Eos
Brucker (uk)

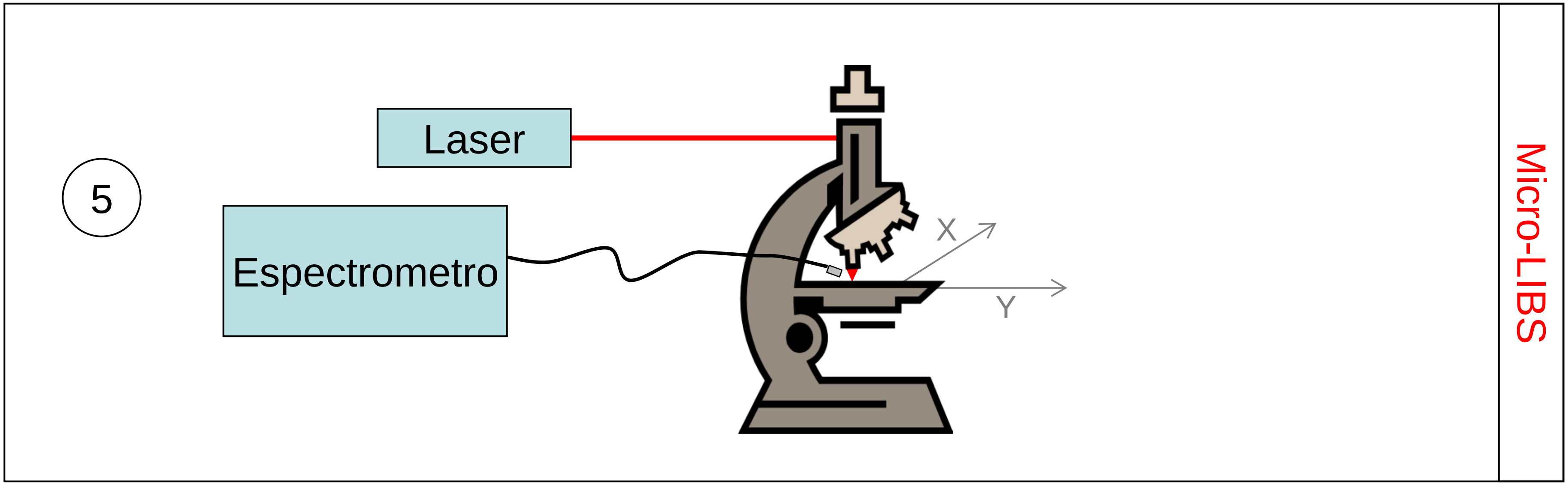
LIBS solution
B&W Tek (usa)

mPulse
Oxford (usa)

Chemlite
TSI (usa)

LIBZ
Sciaps (usa)

MICRO MAPPING



MEEP
IVEA (fr)

APPLICATIONS

Main domains of applications:

Industrial process monitoring

Measurement in hostile environment (nuclear, spatial…)

Recycling

Environmental analysis

Artwork

Biological Applications

Micro structure analysis

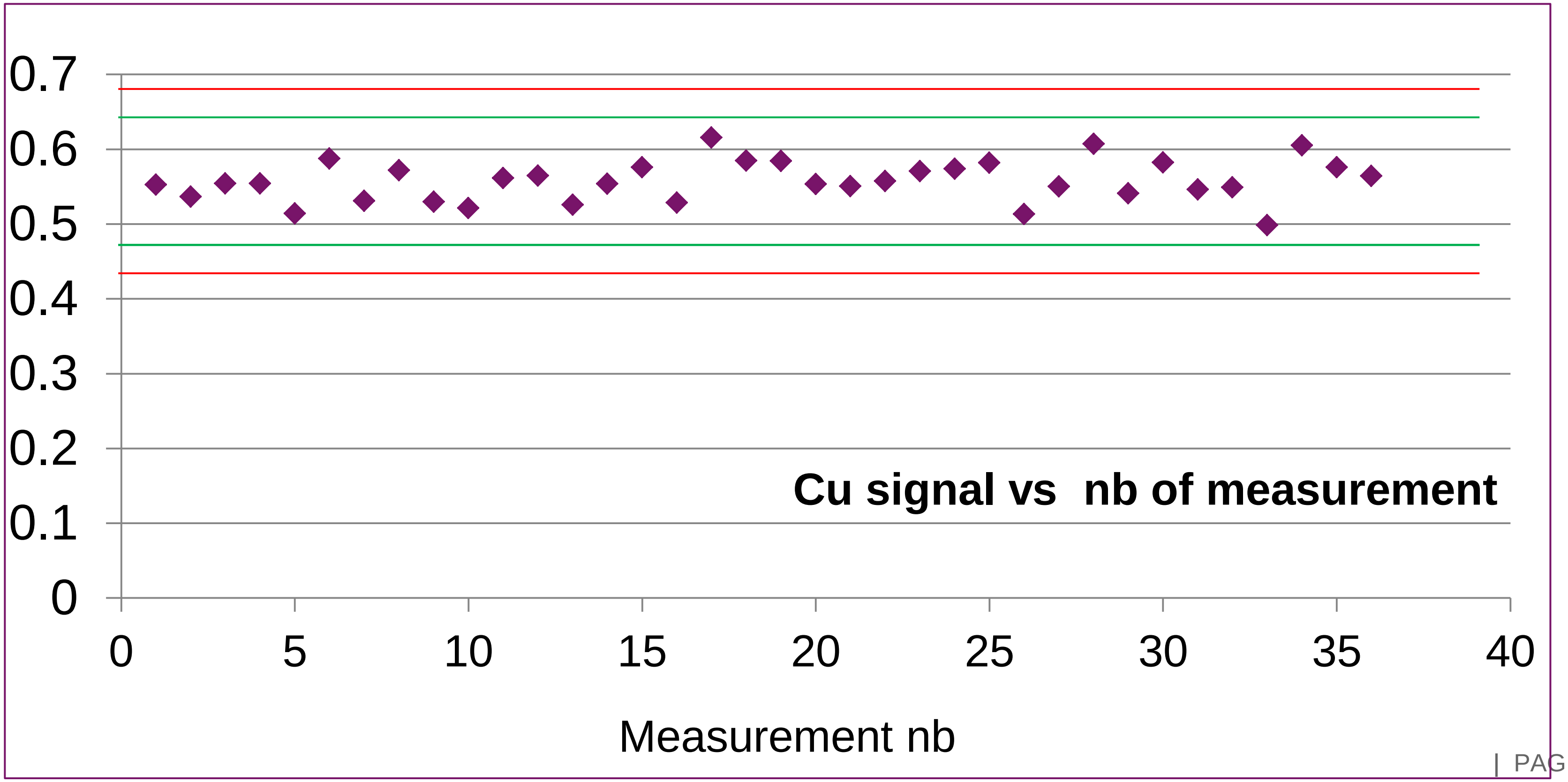
Security (Forensic, NRBCE)

Pharmaceutics and food control

Geological, mine prospection

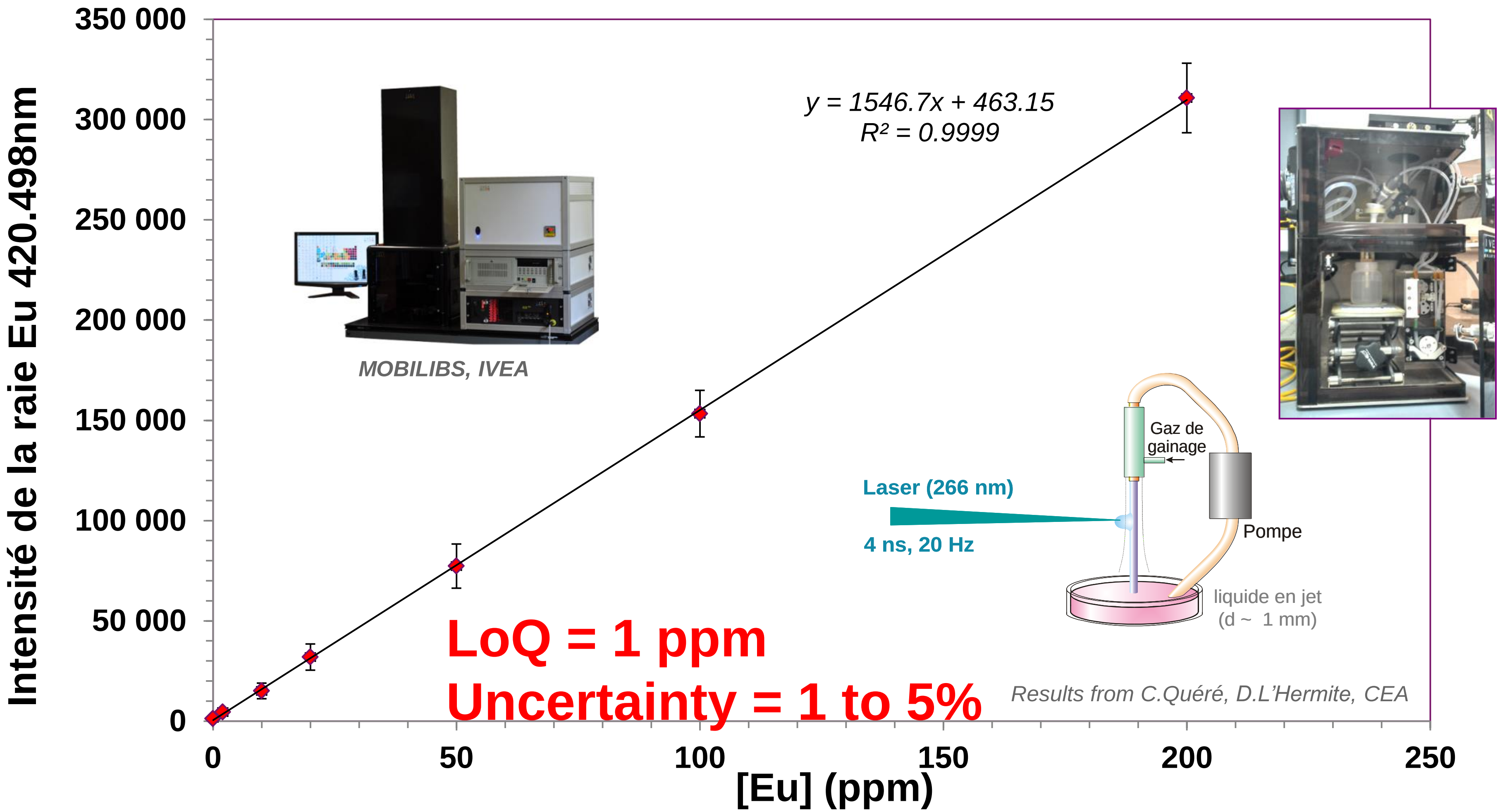
And many others ………….

It is important to verify that the system is operational for measurement → we may use a reference sample



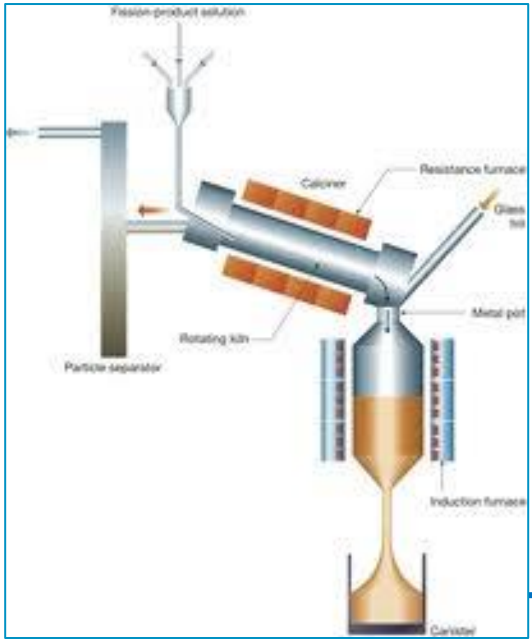
Results from C. Roche CEA-AREVA

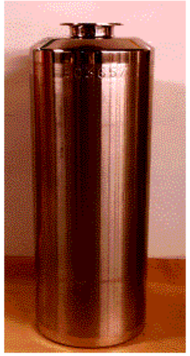
EXAMPLE 1: MEASUREMENT ON LIQUID



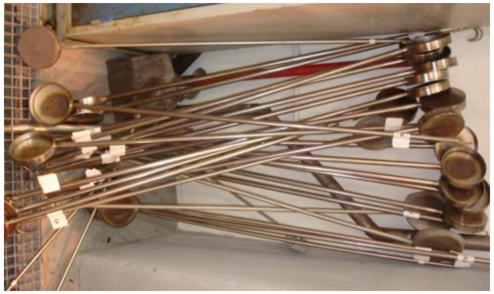
- The good linearity is not due to chance and is not an arrangement of data
- An ideal sample and an equipment with good repeatability

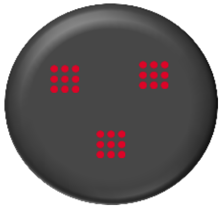
EXAMPLE 2 : VITRIFICATION OF NUCLEAR WASTE

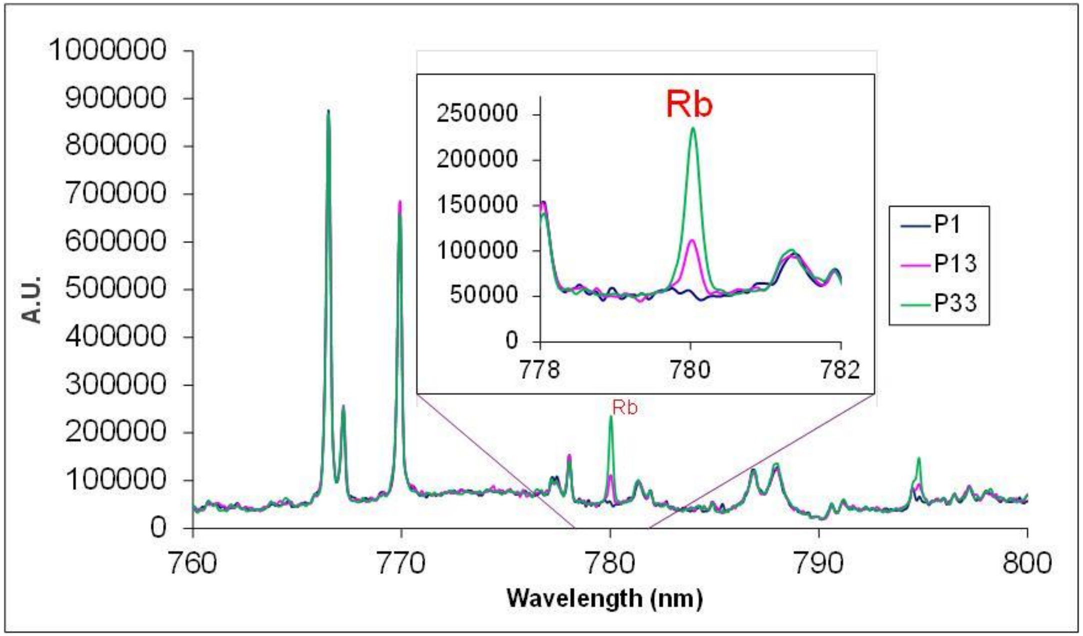




Goal : trap the nuclear waste in glass (chemically very stable) for long time





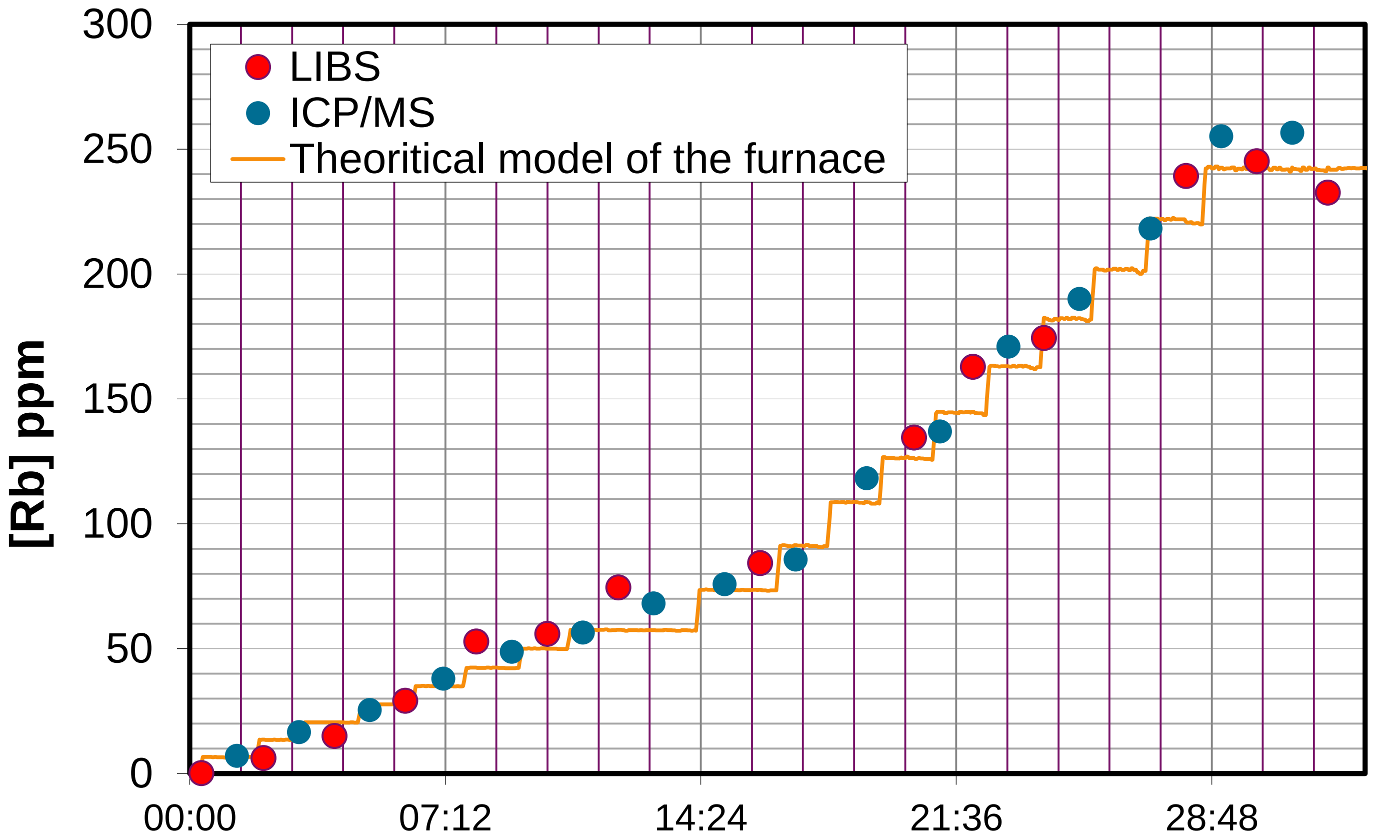


MOBILIBS, IVEA (fr)

Results from E. Sauvage, C. Roche CEA

EXAMPLE 2 : VITRIFICATION OF NUCLEAR WASTE

Comparison LIBS vs ICP/MS



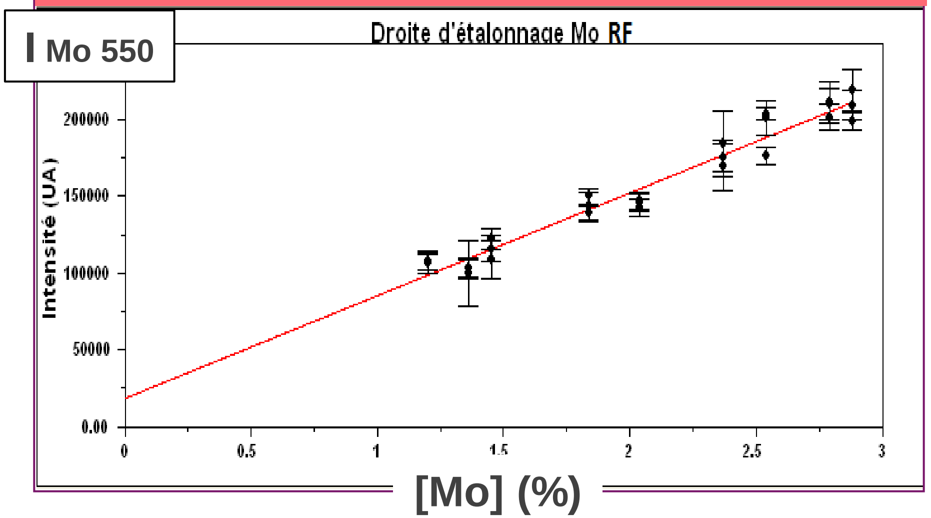
Results from E. Sauvage, C. Roche CEA

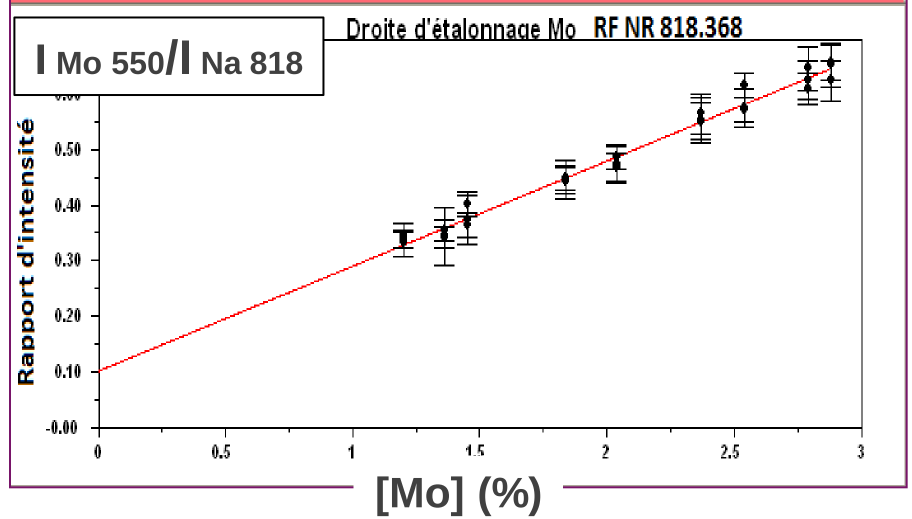
- **Good agreement between ICP-MS and LIBS (<8%)**
- **Time of analysis : LIBS : few hours**
  ICP-MS : 6 months

EXAMPLE 2 : VITRIFICATION OF NUCLEAR WASTE

Mo quantification in the glass

Without normalization	With normalization by Na line





	FX values (Reference)		Without normalisation		With normalisation	
SAMPLE	MoO3 (%)	Na2O (%)	MoO3 (%)	deviation (%)	MoO3 (%)	deviation (%)
C3	2,88	9,54	2,75	**4,51**	2,67	**6,96**
C4	2,79	9,54	2,77	**0,72**	2,76	**1,08**
C6	1,84	9,67	1,75	**4,89**	1,77	**3,80**
C8	1,45	9,83	1,61	**11,03**	1,50	**3,45**

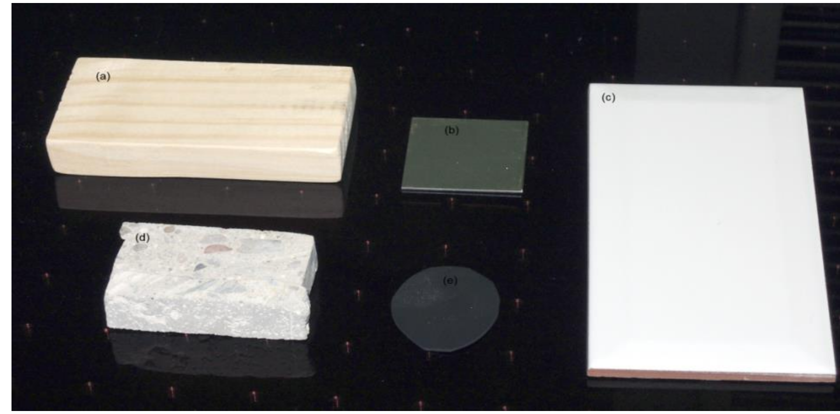
With normalization: deviation <7% between LIBS and XRF

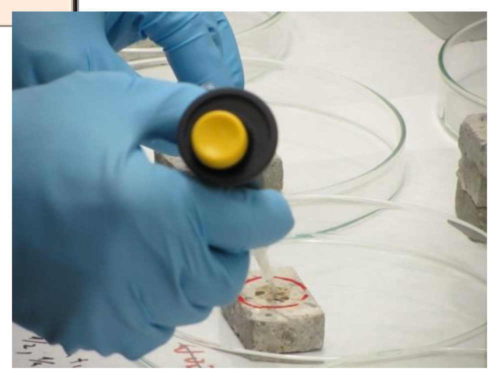
(Usual technique for glass analysis)

Results from, C. Roche CEA-AREVA

EXAMPLE 3 : DETECTION OF CHEMICAL WARFARE AGENT (CWA)

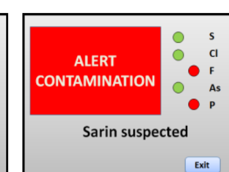
$C_4H_{10}O_2PF$ $C_7H_{16}O_2PF$	Sarin GB Soman GD
$C_5H_{11}O_2N_2P$	Tabun GA
$C_{11}H_{26}O_2NPS$	VX
$C_4H_8Cl_2S$, $S=(C_2H_4Cl)_2$	HD, H
$C_2H_2AsCl)_3$	L





EASYLIBS, IVEA (fr)

Development of a specific data treatment



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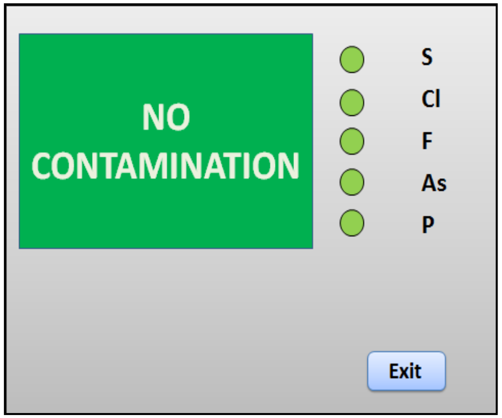
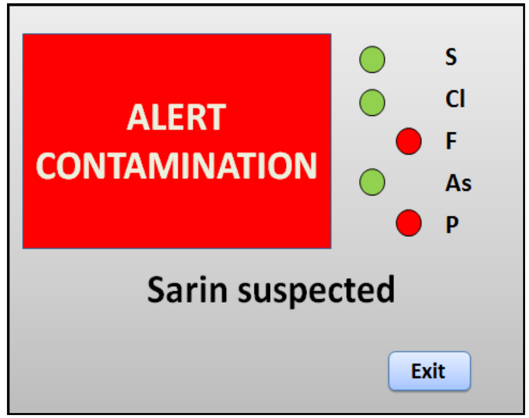




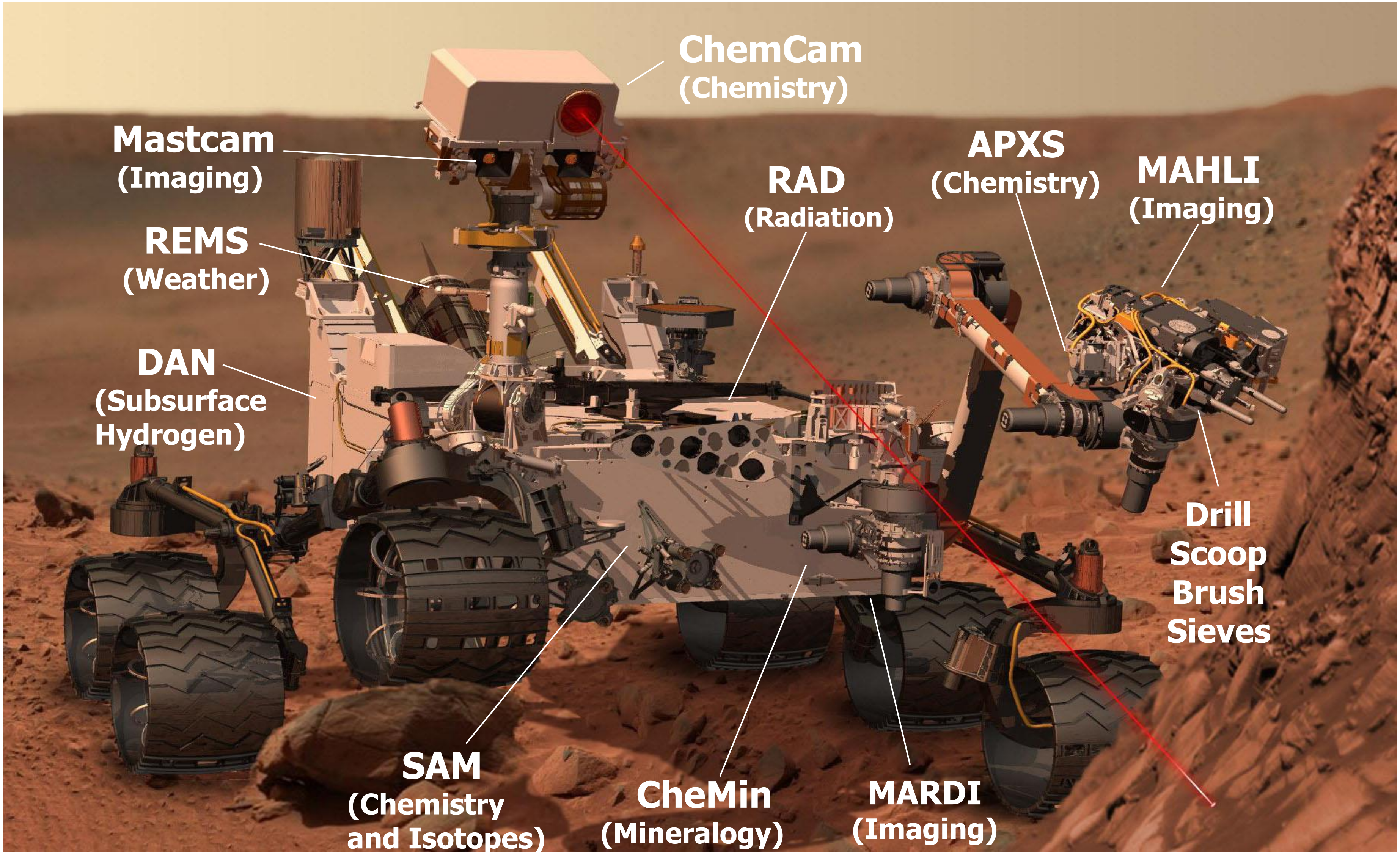
One shot per measurement

Instantaneous response

Rate of good result	HD	L1	VX	GB	Blank
CARC paint	4 / 5	5 / 5	0 / 5	5 / 5	0/5
concrete	3 / 5	5 / 5	0 / 5	4 / 5	0/5
wood	5 / 5	5 / 5	3 / 5	4 / 5	0/5

- **Results are globally ok but not for VX on CARC and concrete**
- **This is due to the high viscosity and low vapor pressure of VX → too amount of liquid → difficult to make a plasma with handable LIBS system**

EXAMPLE 4 : CHEMCAM (CURIOSITY) ON MARS



EXAMPLE 4 : CHEMCAM (CURIOSITY) ON MARS

- Feasibility to do LIBS on Mars was carried out in our laboratory (2002) (CEA Saclay, France)

CEA Saclay; DPC/SEARS/hall 15

EXAMPLE 4 : CHEMCAM (CURIOSITY) ON MARS

Image credit NASA/JPL

- ❑ **Works since august 2012 (more than 3 years without problem)**
- ❑ **Displacement : 7 km**

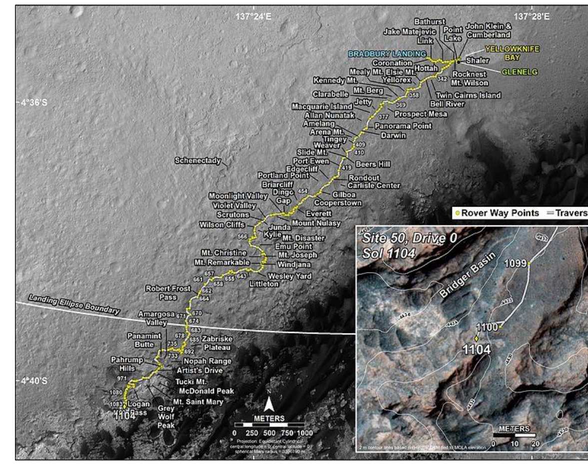
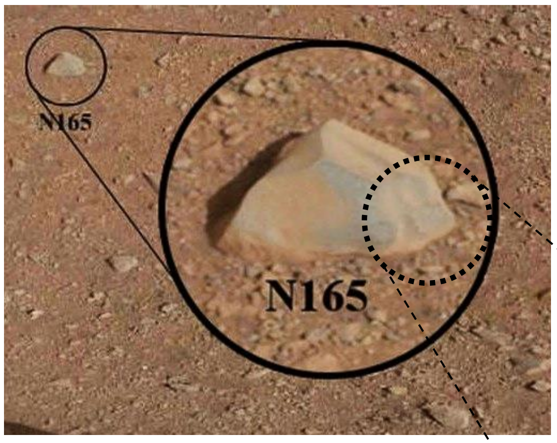


Image credit NASA/JPL

- ❑ **Chemcam is the instrument which works the more (~ every day)**
  - ❑ **λ=1067 nm**
  - ❑ **Train of pulses (50) (remove dust)**
  - ❑ **15mJ /pulse**
  - ❑ **Working distance (1,5 to 7m)**

EXAMPLE 4 : CHEMCAM FIRST SPECTRUM

LIBS works well on Mars and helps geologist



Frist rock analysed by ChemCam on Mars : Coronation

It wasn’t a interesting rock but just to the system

Crédit images : NASA/JPL-Caltech/MSSS/LANL/CNES/IRAP

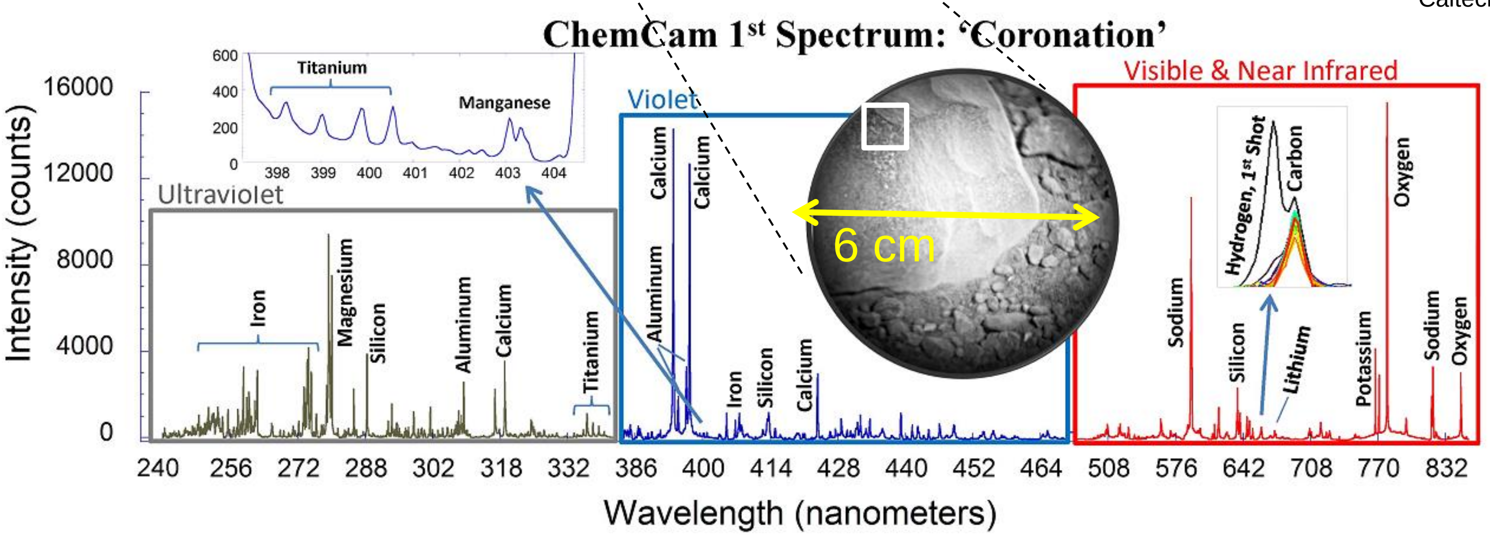
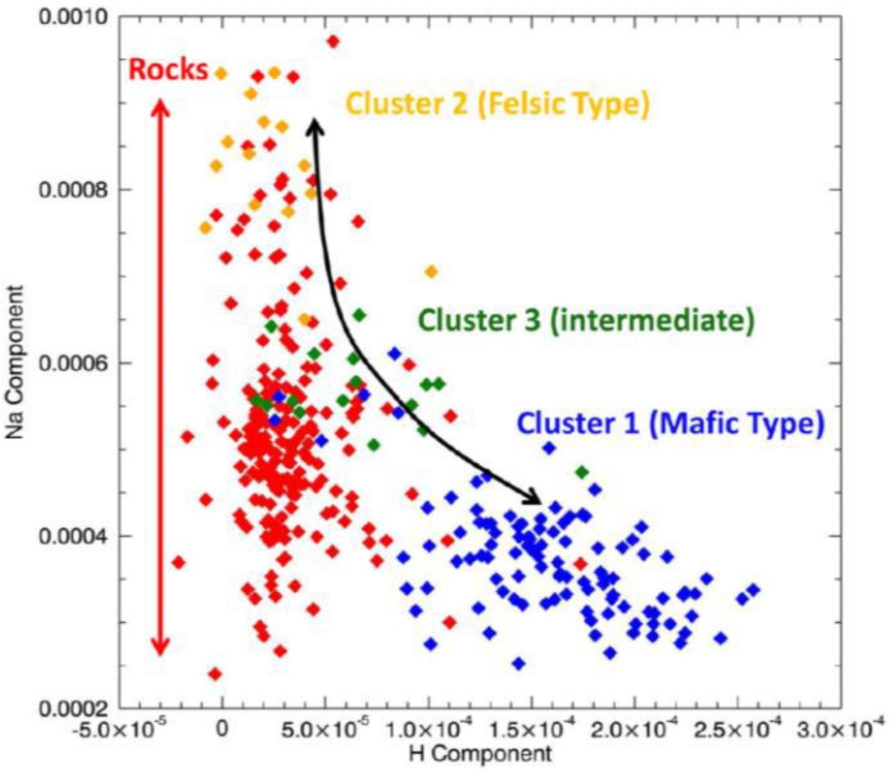
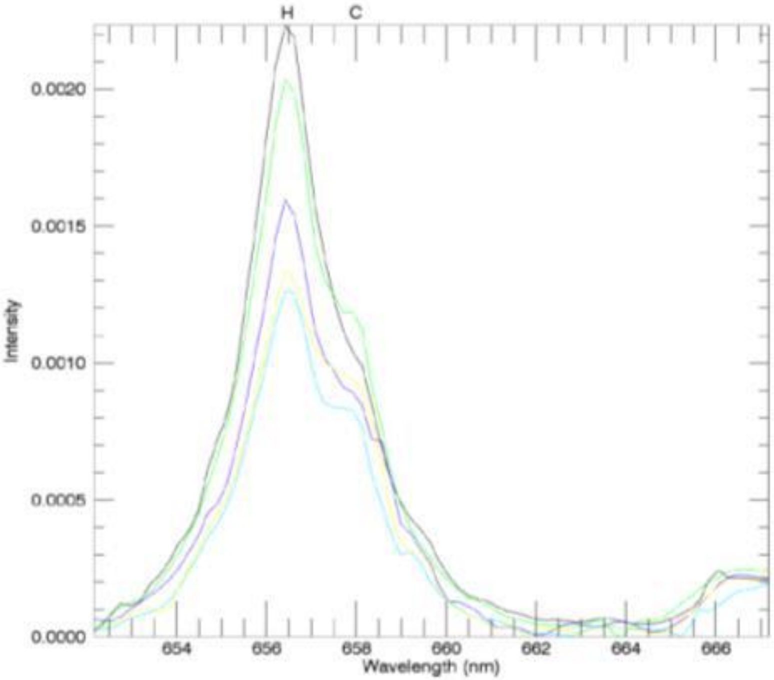


Image credit NASA/JPL

CHEMCAM MAIN RESULTS

❑ Hydrated soil and dust





http://pds-geosciences.wustl.edu/workshops/ChemCam_Workshop_Mar14.htm

Image credit NASA/JPL

First Mars fluorine chemistry

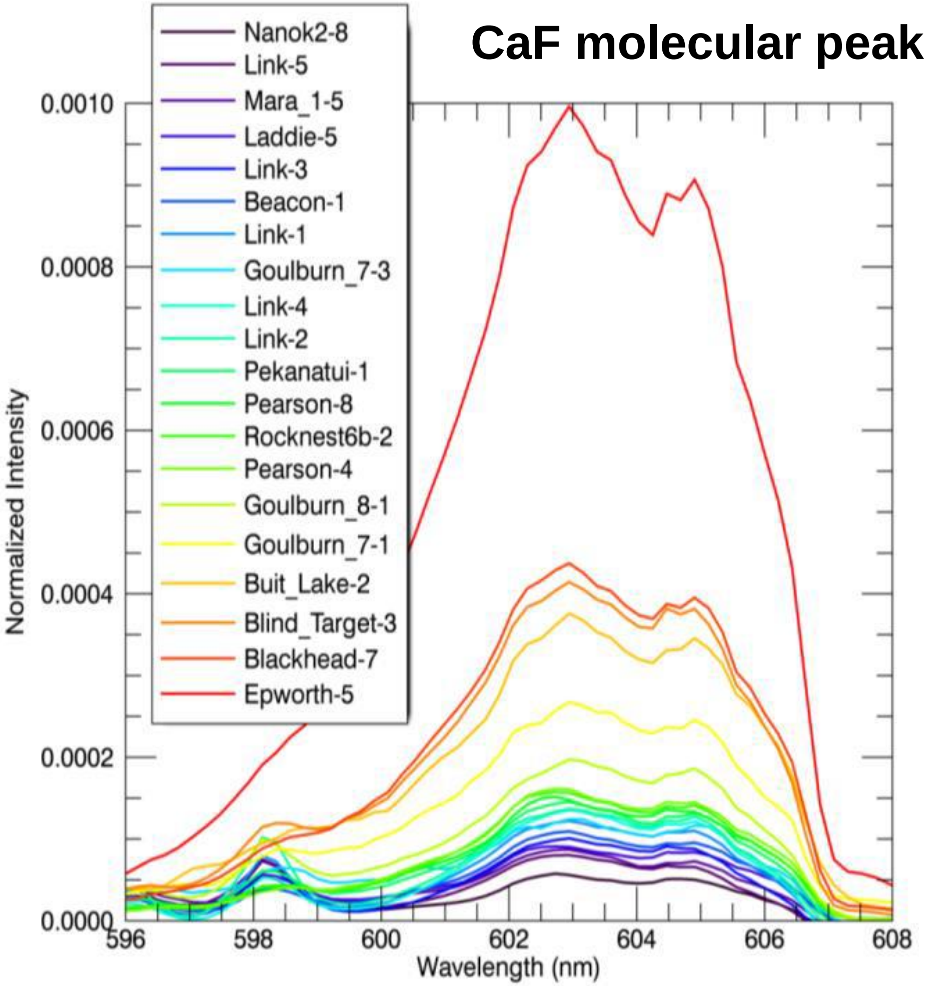


Image credit NASA/JPL

CHEMCAM MAIN RESULTS

❑ First manganese-rich minerals

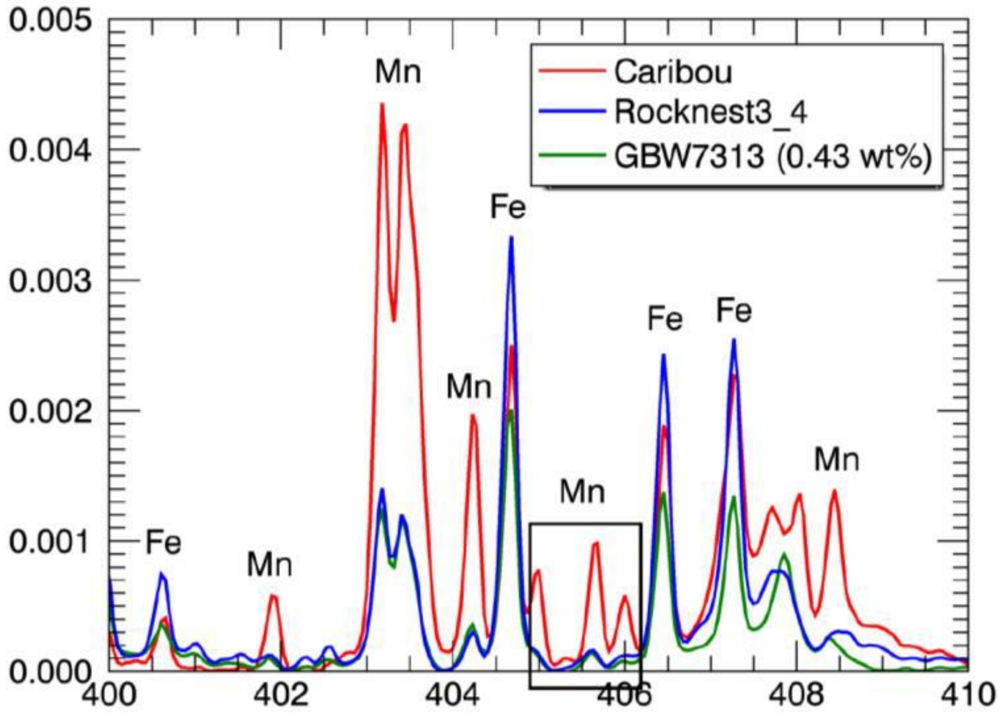


Image credit NASA/JPL

CHEMCAM MAIN RESULTS

❑ First Li, Rb, Sr, and Ba on Mars

- •These elements have generally never been seen on Mars before and they each have implications for Mars geochemistry.
- •Lithium is a strong indicator of alteration;
- •Rb, Sr, and Ba each tend to be sequestered in different minerals:
- •Rb in anorthoclase,
- •Sr in albite and more so in anorthite, etc.
- •The global Rb/K ratio has important implications for planetary origins.

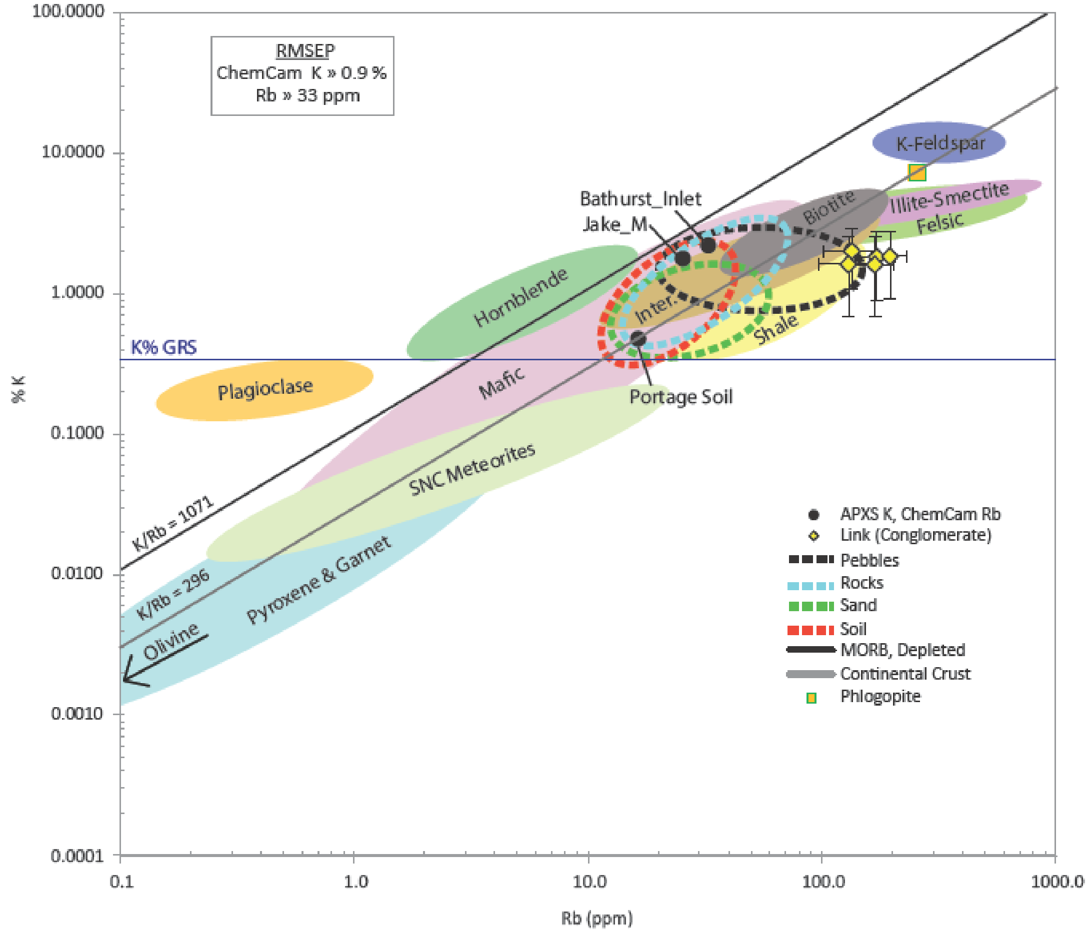


Image credit NASA/JPL

❑ Rock surface alteration of mobile elements

The gradient was consistent among all observed elements, definitively showing relatively recent rock surface alteration

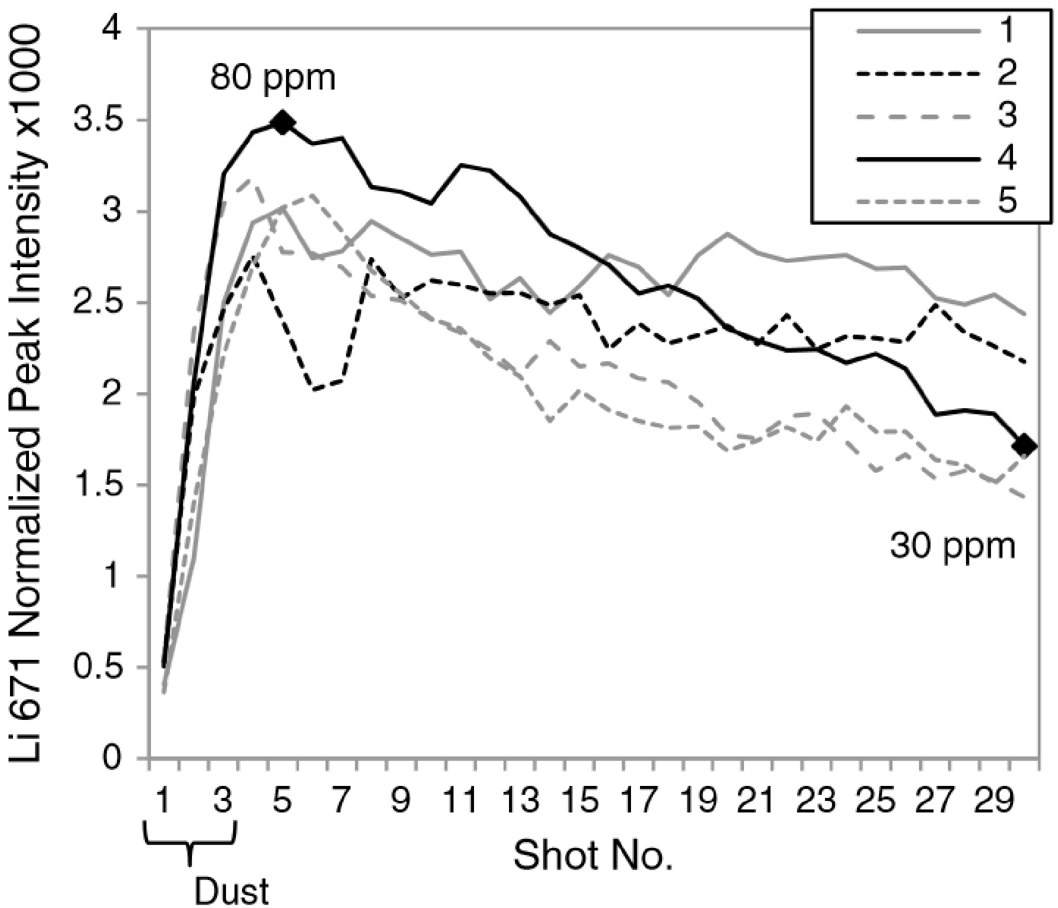


Image credit NASA/JPL

CHEMCAM MAIN RESULTS

- Fe-rich cements in sediments

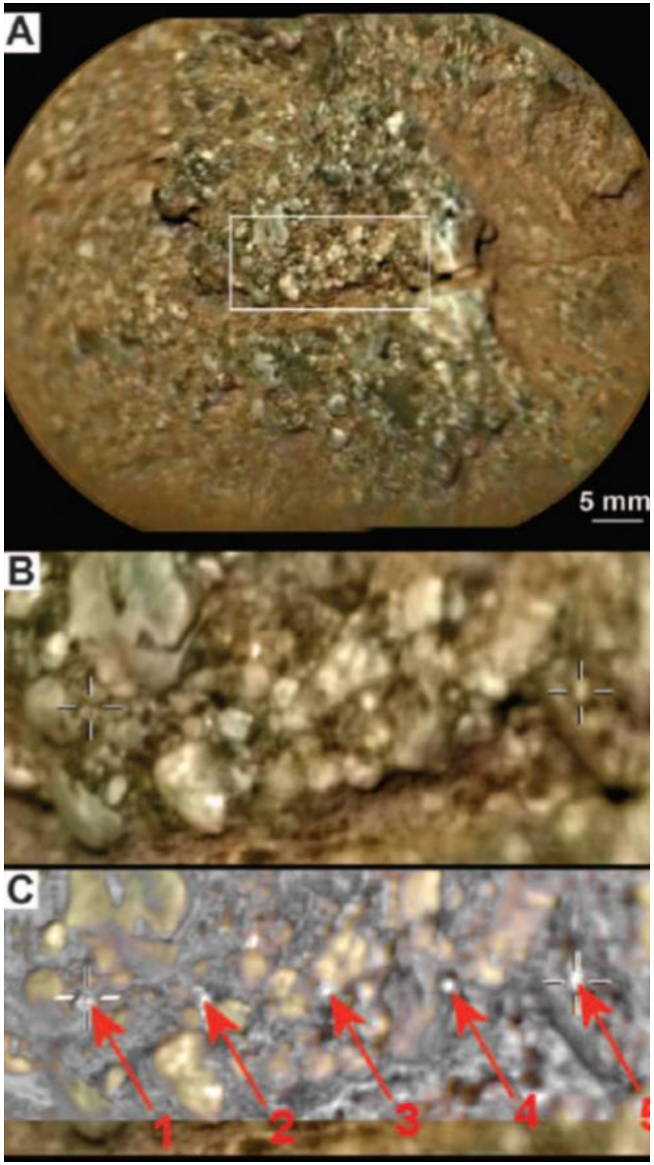
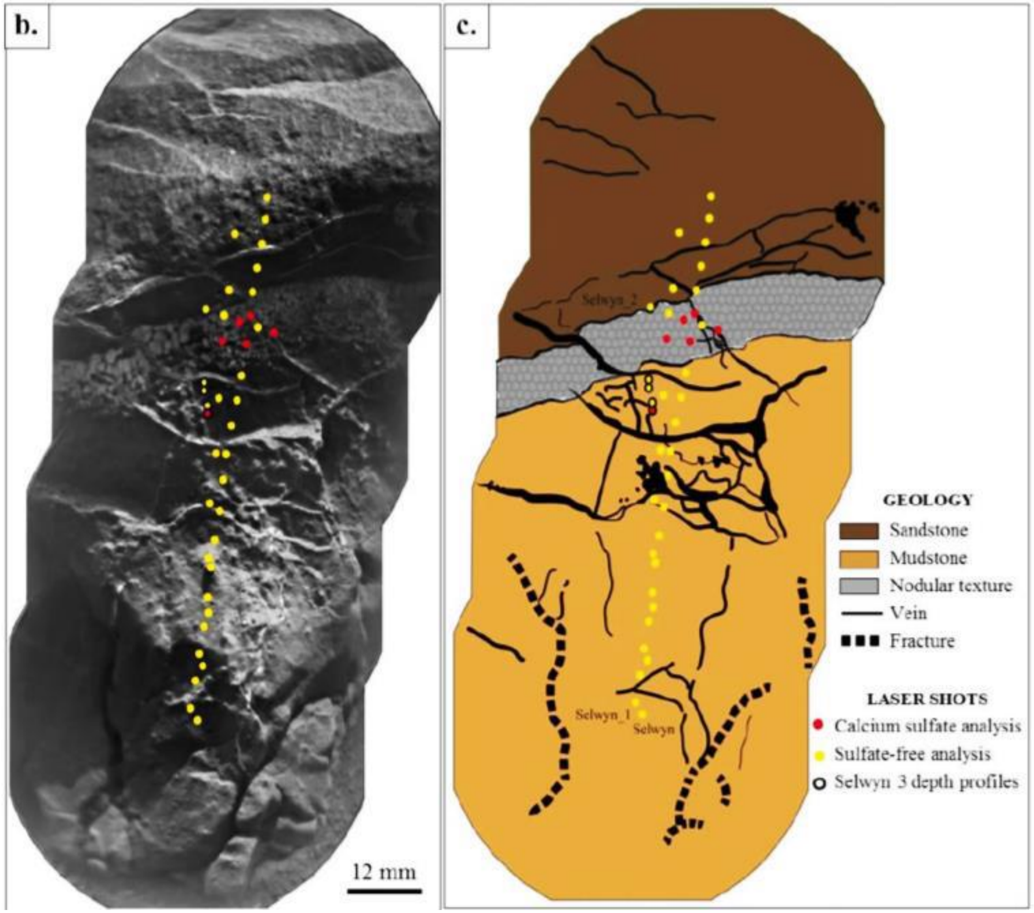


Image credit NASA/JPL

❑ Ca-sulfate veins, variable hydration



ChemCam was the first to observe and confirm the composition of the calcium sulfate veins in the Yellowknife Bay units. We were also able to show that the veins were variably hydrated

Image credit NASA/JPL

Chemostratigraphy with ChemCam


Last Curiosity selfie

Image credit NASA/JPL

And it still continues …

DE LA RECHERCHE À L'INDUSTRIE

OUR LIBS TEAM

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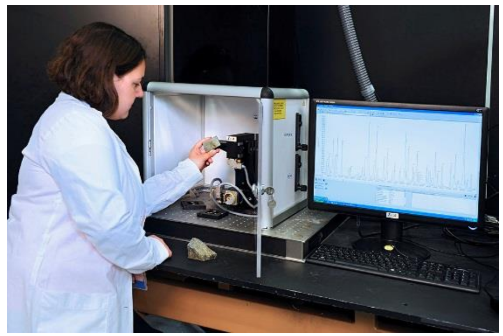

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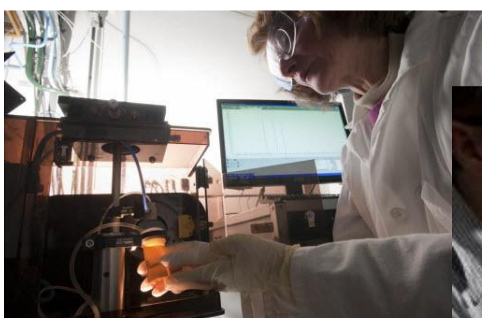

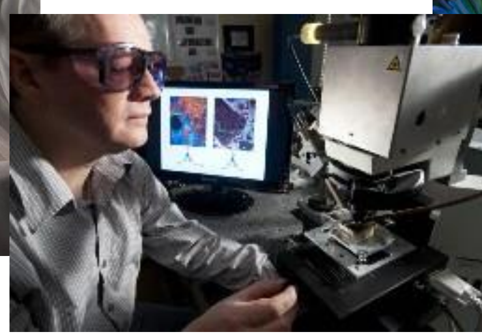

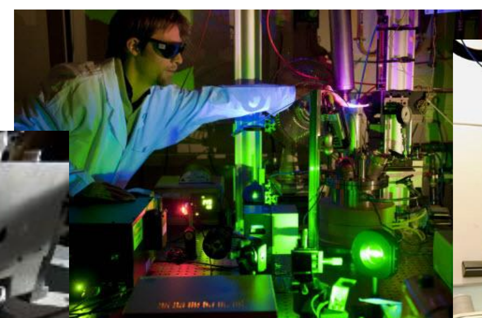

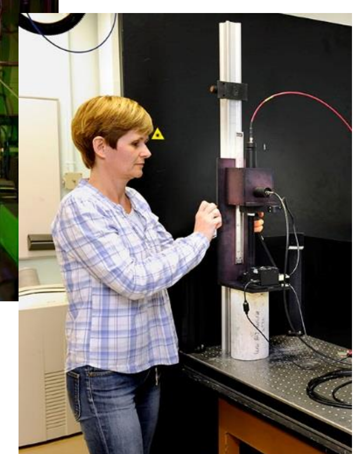

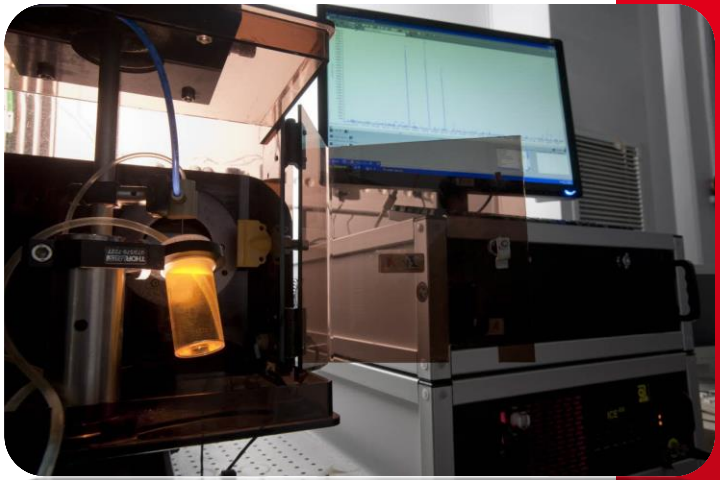

Thank's for your attention

Muchas gracias por su atención

Merci pour votre attention

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