Raman spectroscopy

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Instituto Nacional de Técnica Aerospacial

NASA Astrobiology Institute

Motivation

Raman spectroscopy experienced an enormous expansion in the last decades and it is widely used in many applications today because the capability to precisely identify molecular compounds (solid, liquid or gases), mineral phases, etc. And in general structural features in the materials.

Raman spectroscopy has several important advantages:

No sample preparation is needed

Non destructive analysis

Very fast acquisition data

Micro-macro modes

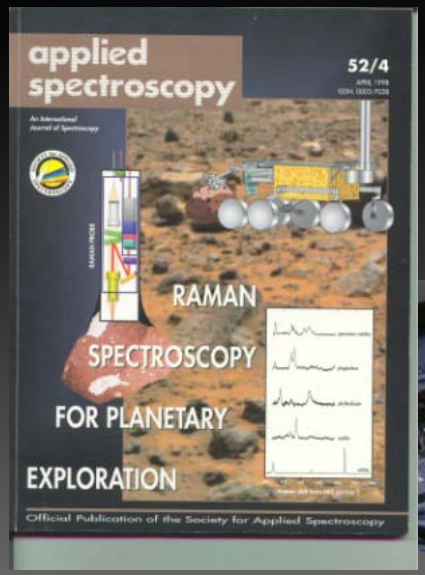
Contac-remote modes

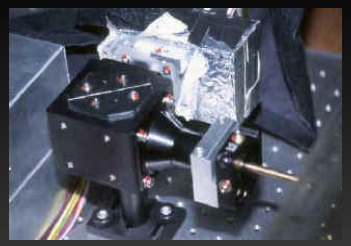
Capability to combine with other techniques in a single instrument

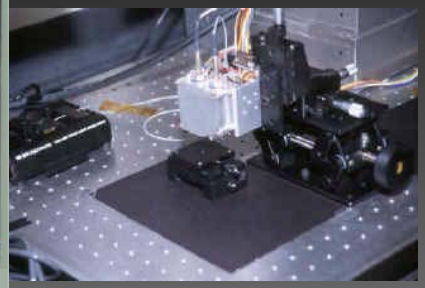
All these characteristics leaded to the idea that Raman spectroscopy could be a powerful technique for planetary exploration and in particular for detailed surface analysis on Mars

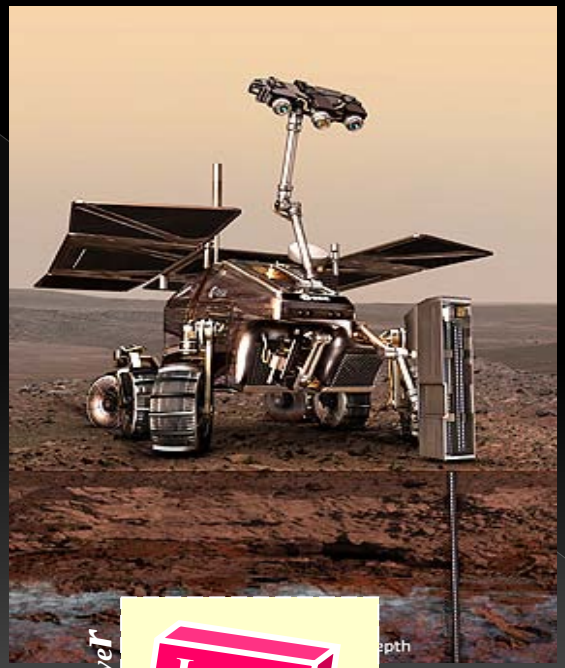
Former developments

Instrument for MER
1998 Larry Haskin A. Wang





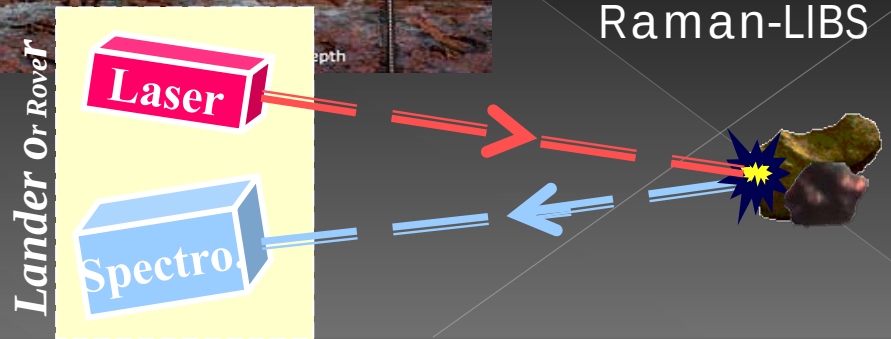




EXLIBRIS Project / Exomars

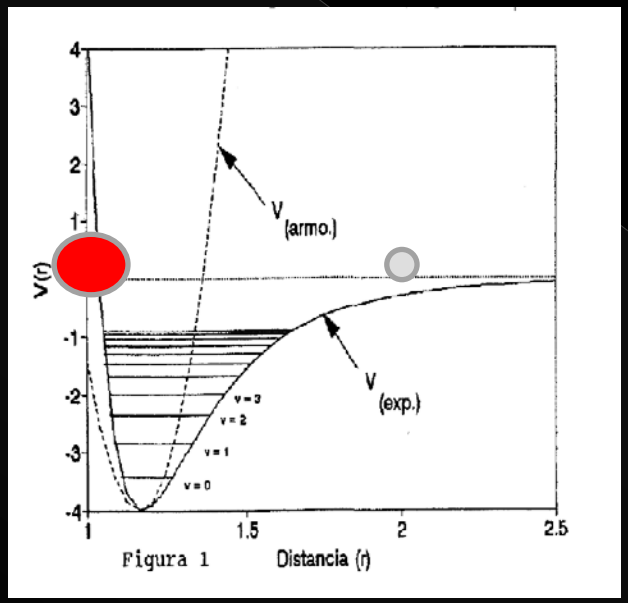
(F. Rull & S. Maurice, 2003)

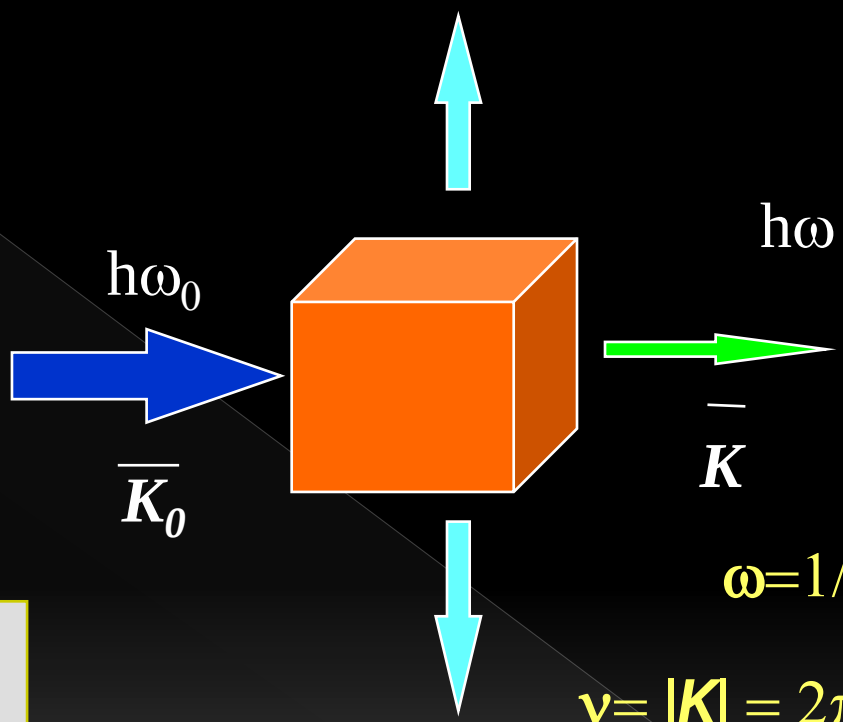
Raman-LIBS



The Raman effect ?

The matter is intrinsically DYNAMICS





λ / cm

ω / s^{-1}

$|K| = 2\pi/\lambda$ (cm^{-1})

$\omega = 1/T = c/\lambda$

$\nu = |K| = 2\pi/\lambda = 2\pi\omega/c$

- $V(r) = -A/r^m + B/r^n$

$$V(r) = k\, r^2/2$$

$$T = E + V$$

$$\omega = 1/2\pi(k/\mu)^{1/2}$$

$$h\omega_0 = h\omega \text{ (Elastic)}$$

$$|K_0| = |K|$$

Classical Approach to the Raman effect

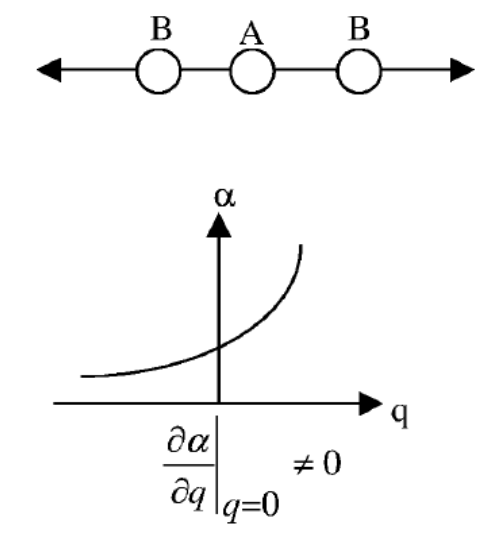
When a molecule is subjected to the electric field $E = E_0 \cos\omega t$ of electromagnetic radiation, the dipolar moment of the molecule p is given by:

$$p = \mu_0 + [\alpha]E$$

If the movement is described by $q_n(t) = q_{n0}\cos(\omega_n t)$,

$$p = \mu_0 + \alpha(0)E_0\cos(\omega t) + \sum_{n=1}^{Q}\left(\frac{\partial\mu}{\partial q_n}\right)_0 q_{n0}\cos(\omega_n t)$$

$$+\frac{1}{2}E_0\sum_{n=1}^{Q}\left(\frac{\partial\alpha}{\partial q_n}\right)_0 q_{n0}\left[\cos(\omega+\omega_n)t + \cos(\omega-\omega_n)t\right]$$



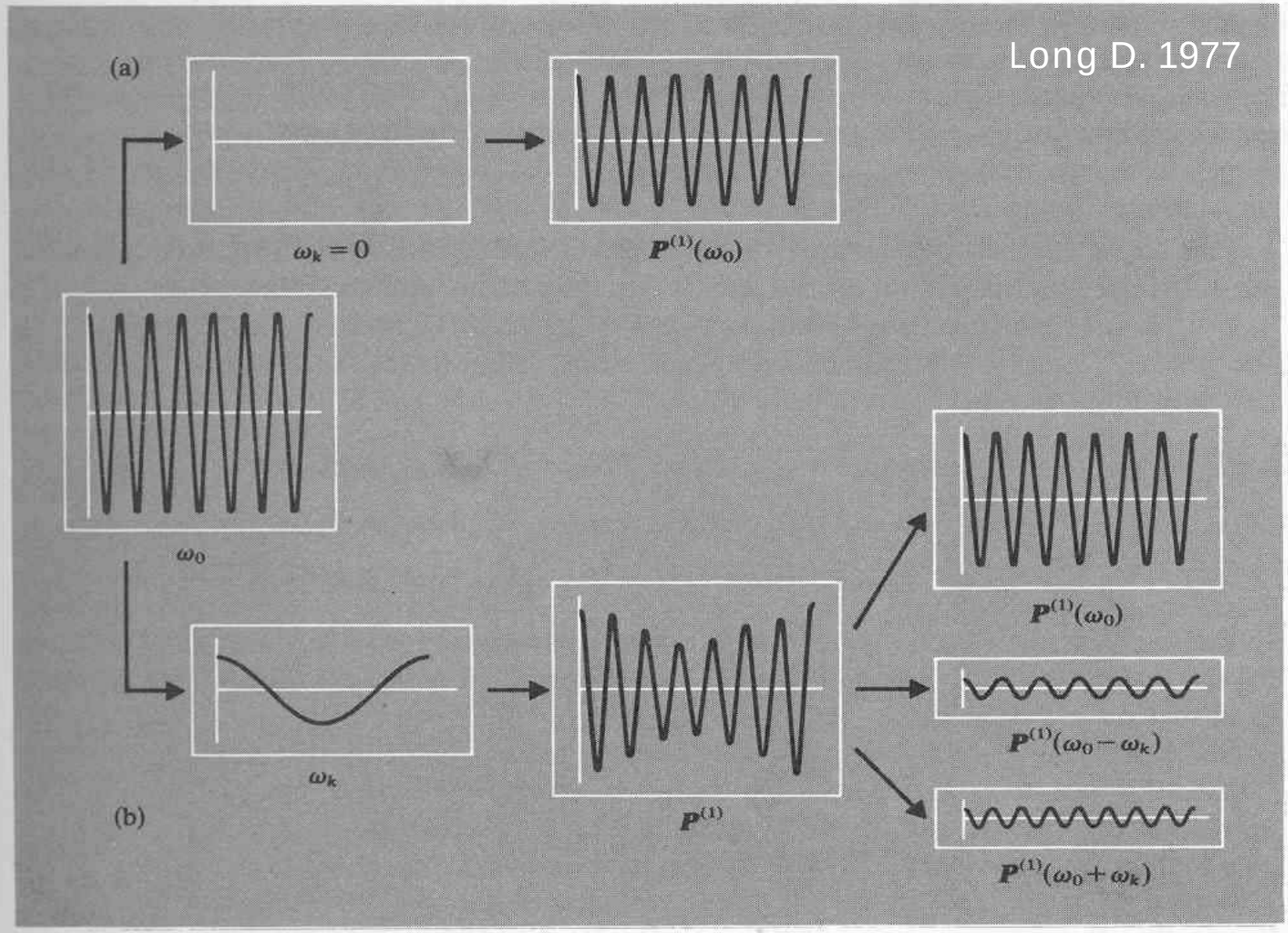
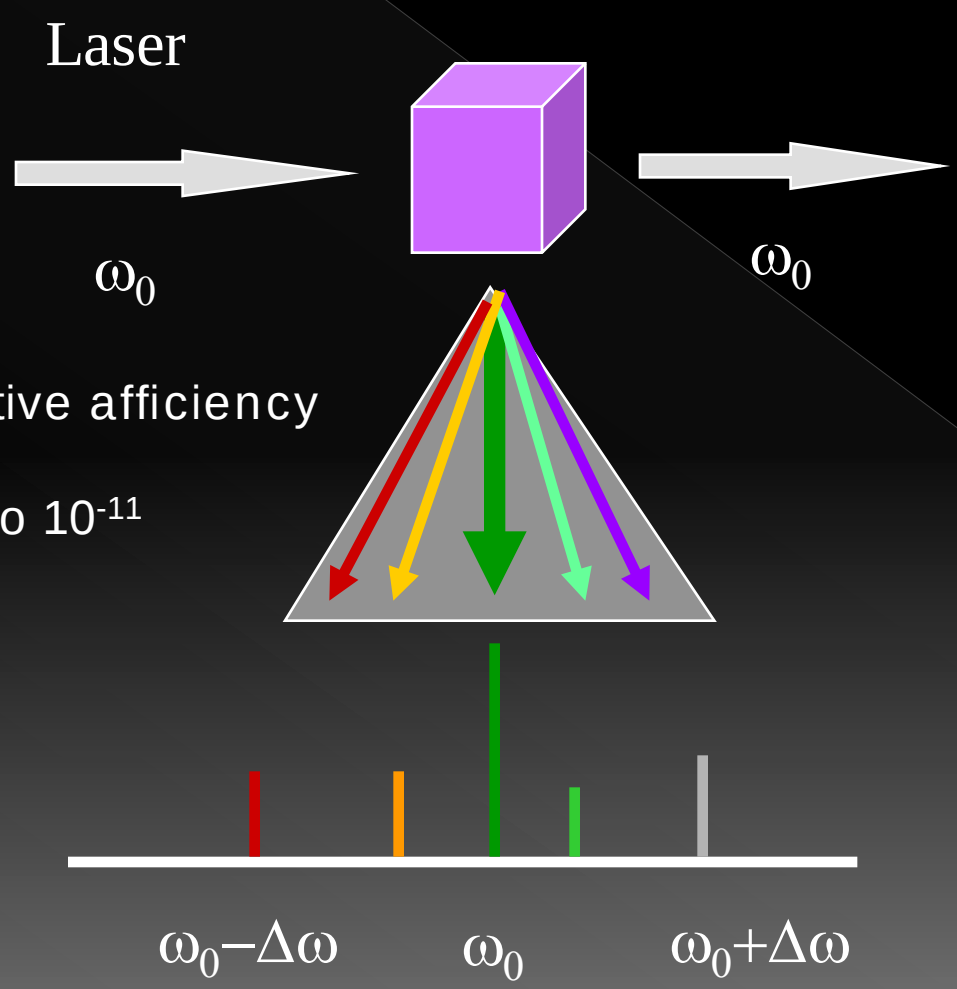


Fig. 3.3 Time dependence of the linear induced dipoles $P^{(1)}$ produced by electromagnetic radiation of frequency ω_0: (a) scattering molecule not vibrating $\omega_k = 0$: $P^{(1)} = P^{(1)}(\omega_0)$; and (b) scattering molecule vibrating with frequency ω_k: $P^{(1)} = P^{(1)}(\omega_0) + P^{(1)}(\omega_0 - \omega_k) + P^{(1)}(\omega_0 + \omega_k)$

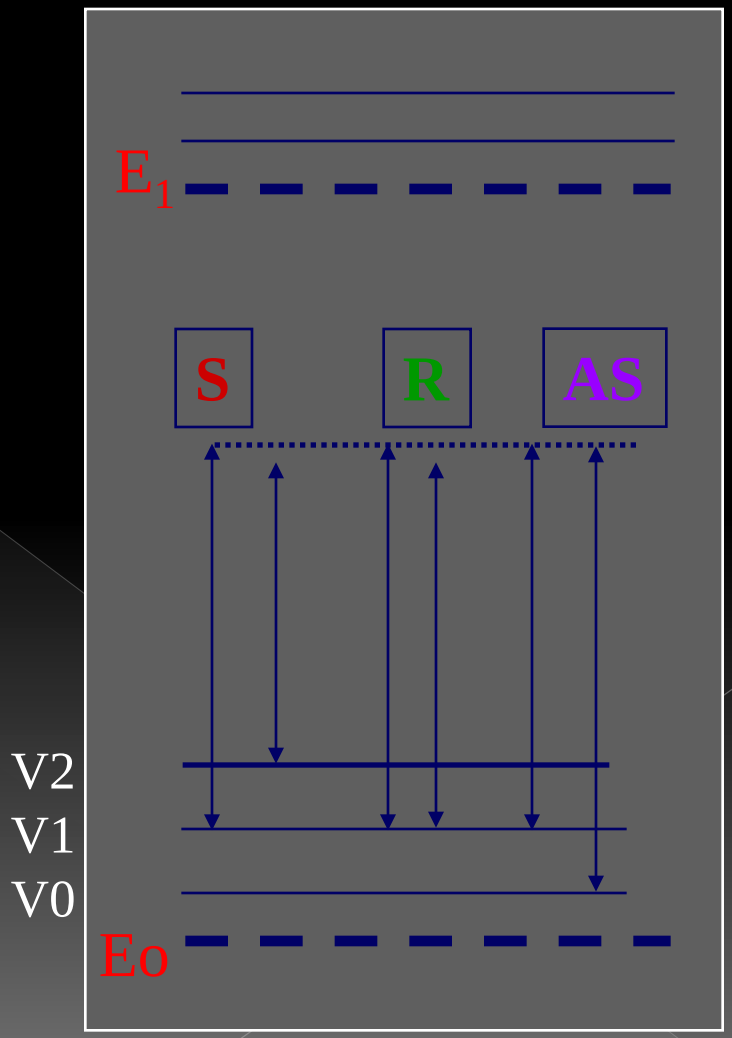
RAMAN Scattering

$$I(v) = K\,[\alpha]^2$$



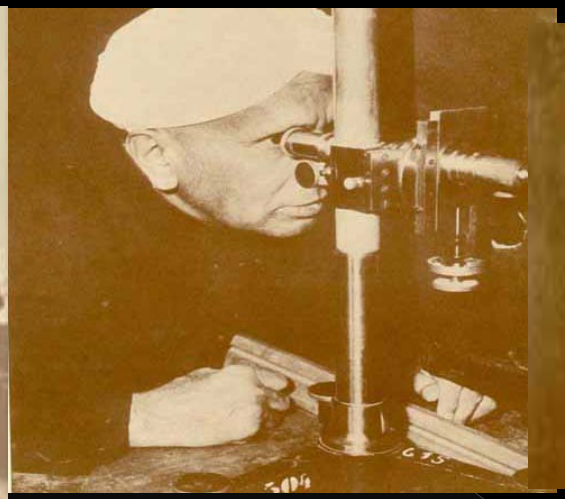
Relative afficiency

10^{-8} to 10^{-11}

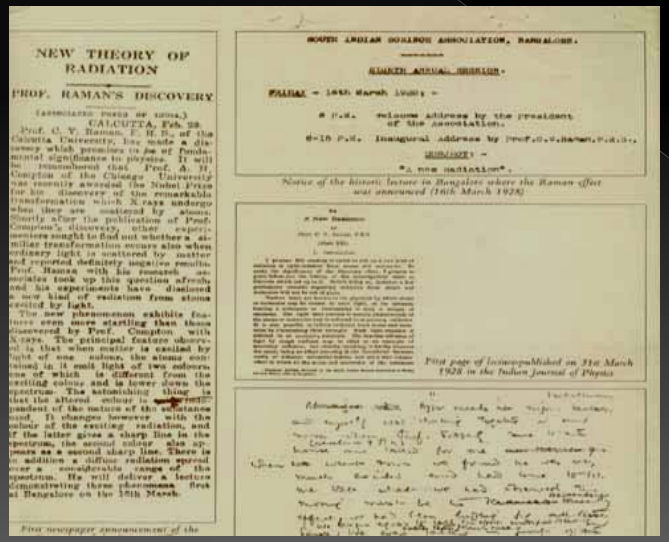


Raman discovered this effect experimentally on 28th February 1928

Raman called this effect "secondary radiation induced by the light"



Nobel Price 1930



NEW THEORY OF RADIATION

PROF. RAMAN'S DISCOVERY

CALCUTTA, Feb. 28

Prof. C. V. Raman, F. R. S., of the Calcutta University, has made a discovery which promises to be of fundamental significance to physics. It will be remembered that Prof. A. H. Compton of the Chicago University has recently awarded the Nobel Prize for his discovery of the remarkable transformation which X rays undergo when they are scattered by atoms. Shortly after the publication of Prof. Compton's discovery, other experimenters sought to find out whether a similar transformation occurs also when ordinary light is scattered by matter and reported definitely negative results. Prof. Raman with his research associates took up this question afresh and his experiments have disclosed a new kind of radiation from atoms excited by light.

The new phenomenon exhibits features even more startling than those discovered by Prof. Compton with X rays. The principal feature observed is that when matter is excited by light of one colour, the atoms contained in it emit light of two colours, one of which is different from the exciting colour and is lower down the spectrum. The astonishing thing is that the altered colour is independent of the nature of the substance used. It changes however with the colour of the exciting radiation, and if the latter gives a sharp line in the spectrum, the normal colour also appears as a second sharp line. There is in addition a diffuse radiation spread over a considerable range of the spectrum. He will deliver a lecture demonstrating these phenomena first at Bangalore on the 16th March.

First newspaper announcement of the

SOUTH INDIAN SCIENCE ASSOCIATION, BANGALORE.

EIGHTH ANNUAL SESSION.

FRIDAY - 16th March 1928 -

8 P.M. Welcome address by the president of the association.

8-15 P.M. Inaugural address by Prof. C. V. Raman, F.R.S.:

SUBJECT: -

"A new radiation".

Notice of the historic lecture in Bangalore where the Raman effect was announced (16th March 1928)

A New Radiation

By

Prof. C. V. Raman, F.R.S.

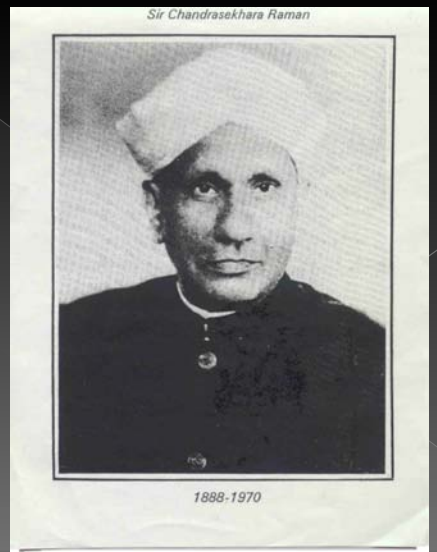
(Received on March 28, 1928)

1. Introduction

First page of letter published on 31st March 1928 in the Indian Journal of Physics

February 28th is the Natioanl Science Day in India

(publication of the discovery in the Calcuta's newspapers on February



The Raman effect:

A “coordinated”discovery ??

From 1913 Mandelstam and Landsgber in Russia performed similar studies using crystals, mainly quartz.

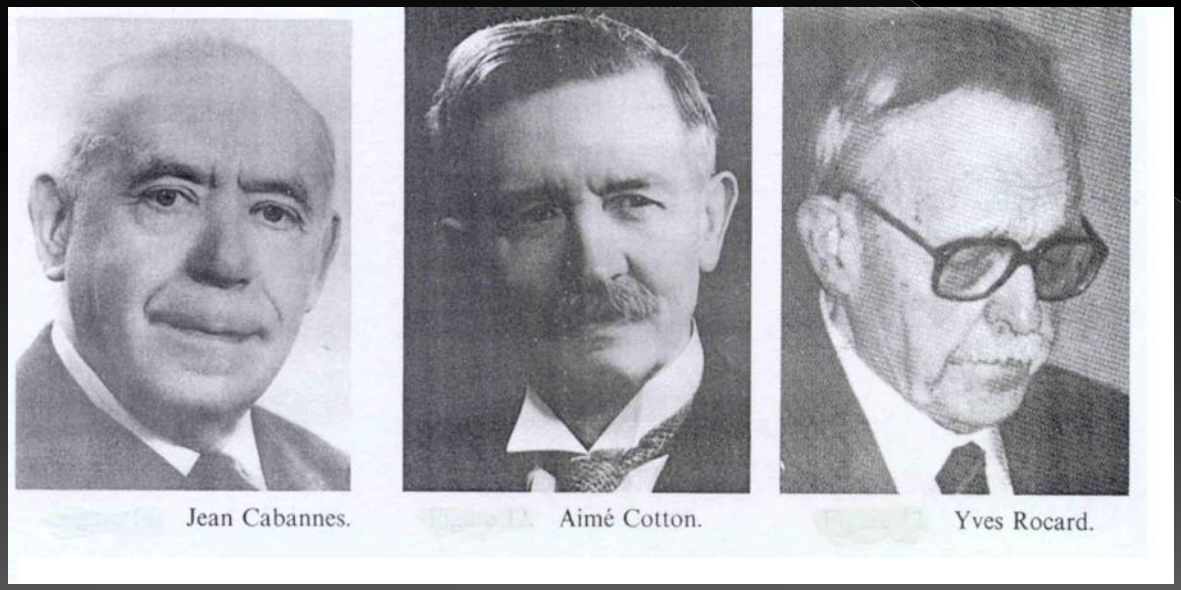
On 21 of February 1928 at the Moscow State University they observed for the first time the “secondary radiation”. But the first publication appears several months later (Naturwissenschaften, on 13 of July).

By that time Raman had performed a worldwide diffusion of the discovery. This was not well accepted by the Soviet system. Mandelstam in particular was punished….

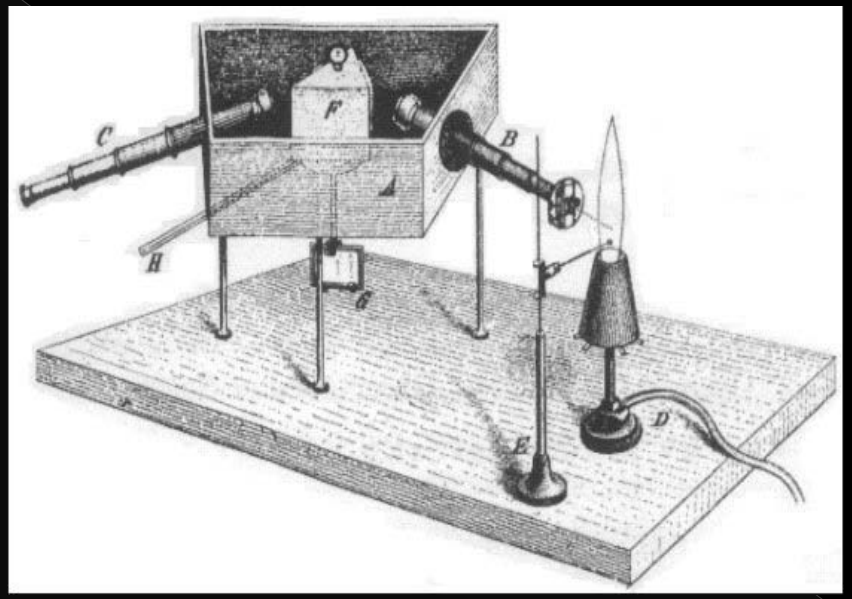
L. I. Mandelstam.

G. D. Landsberg.

Also at that time, several French physicists also studied the scattering of light in gaseous phases.
Mainly: Alfred Kastler, Pierre Daure, Jean Cabannes and Yves Rocard. These three last physicists discover the Cabannes - Daure effect and publish the results in March-April 1928.



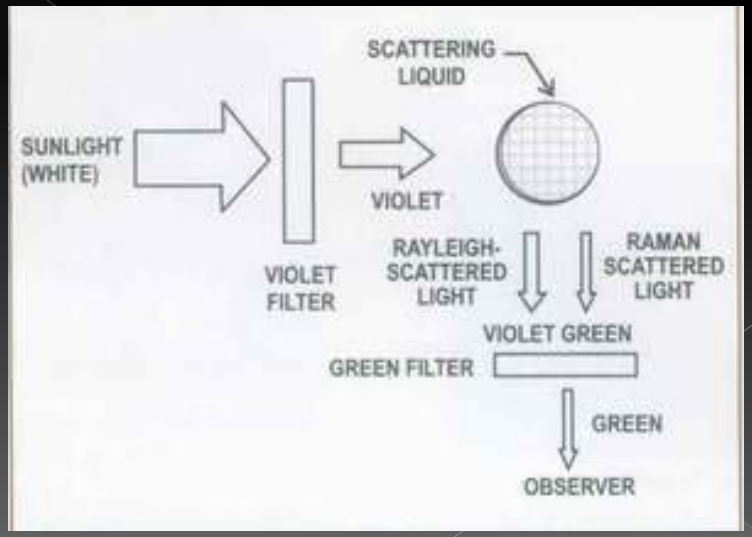
The Raman instruments



Espectrograph_Kirchhoff_Bunsen_1823

First spectrograph used by Raman

Raman spectrum CCl4



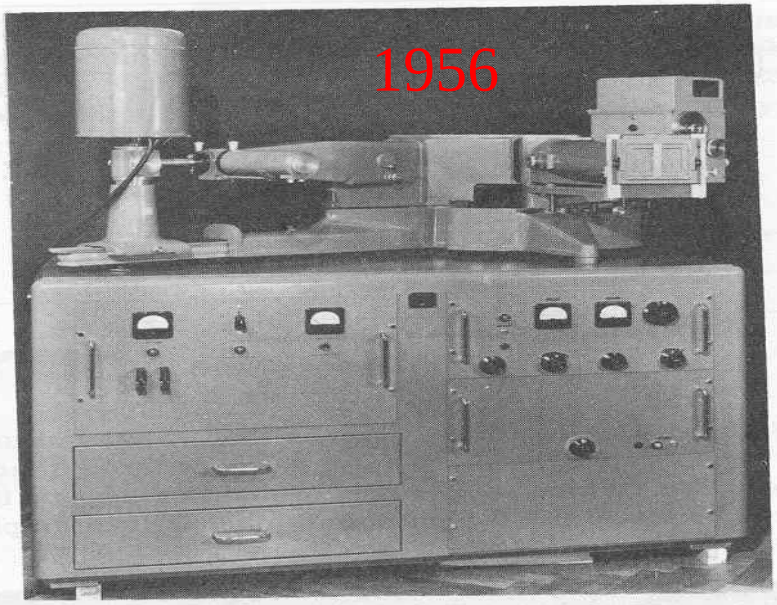


Fig. 1. Hilger E612 Raman spectrometer.

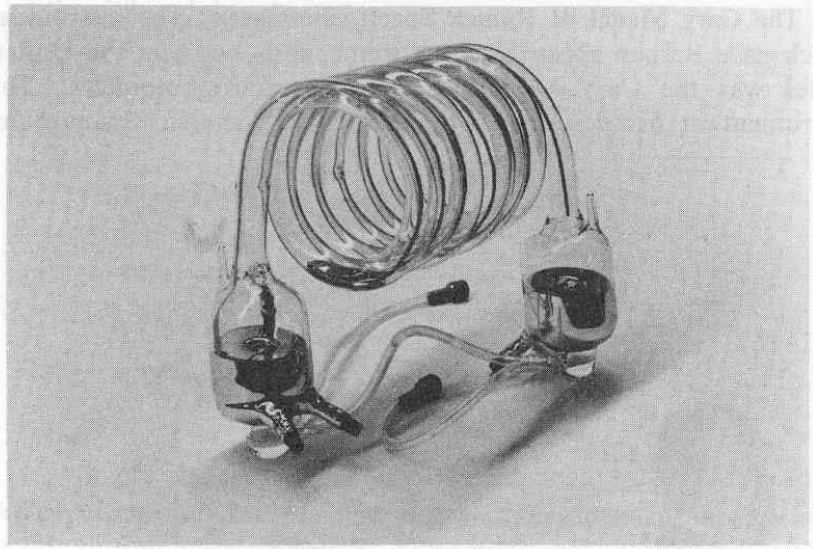
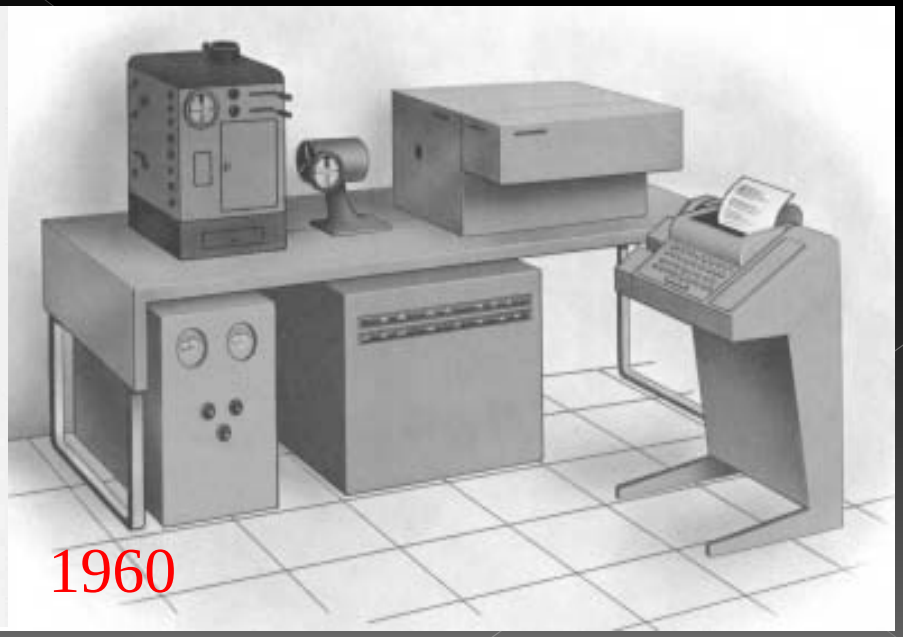
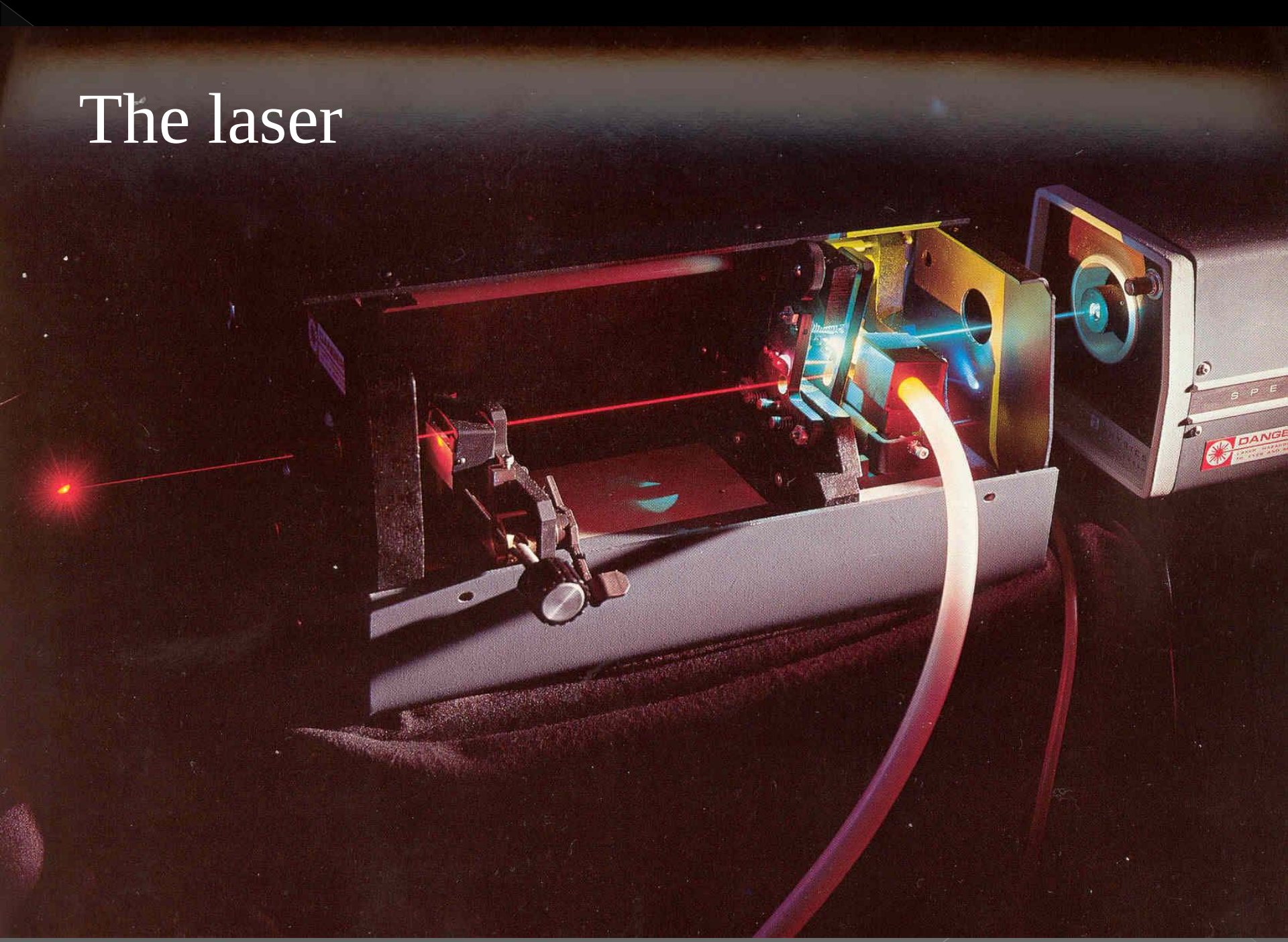
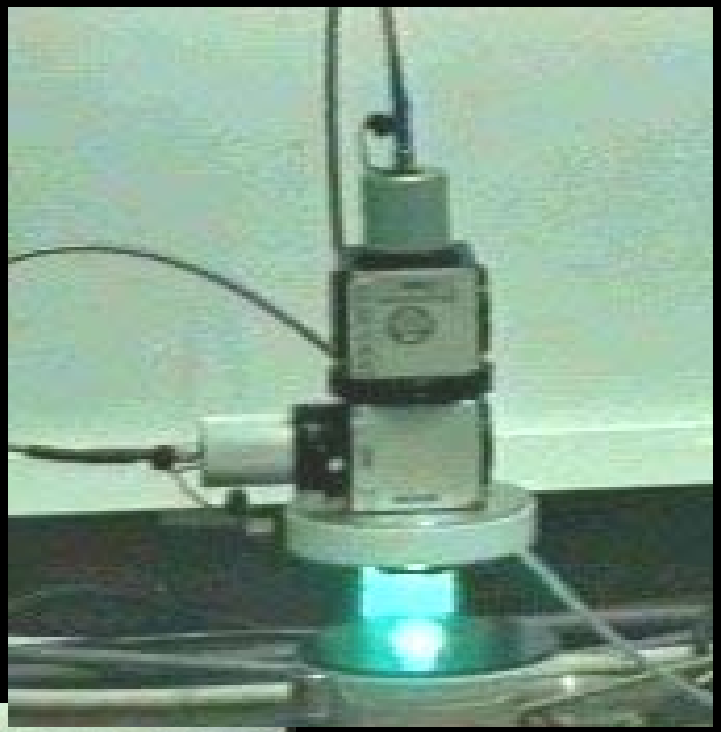


Fig. 5. The mercury arc lamp used in the Cary Model 81.

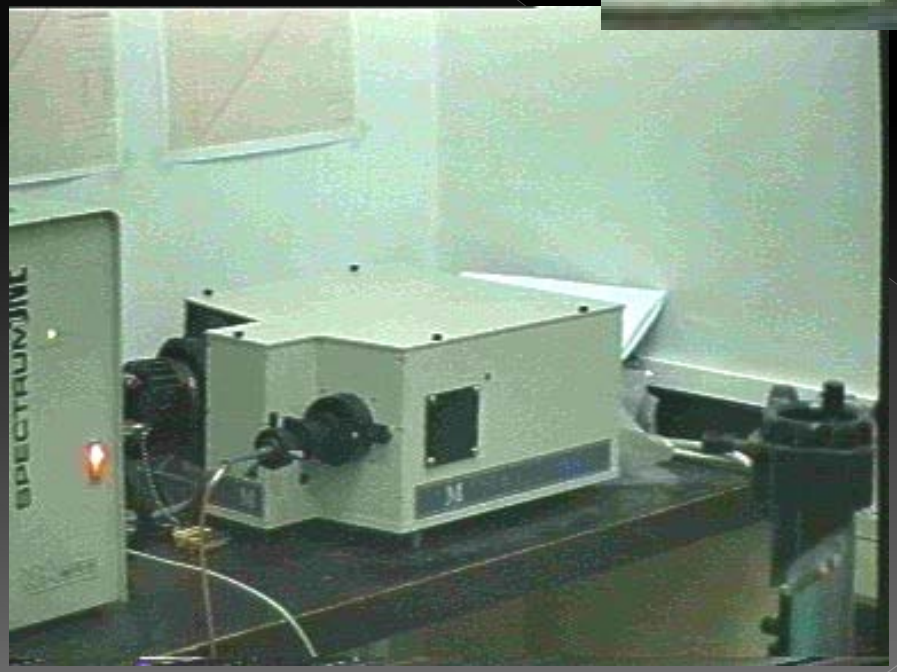


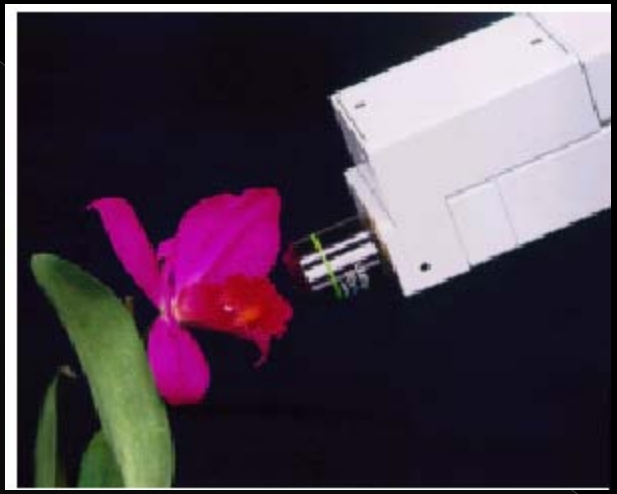
The laser

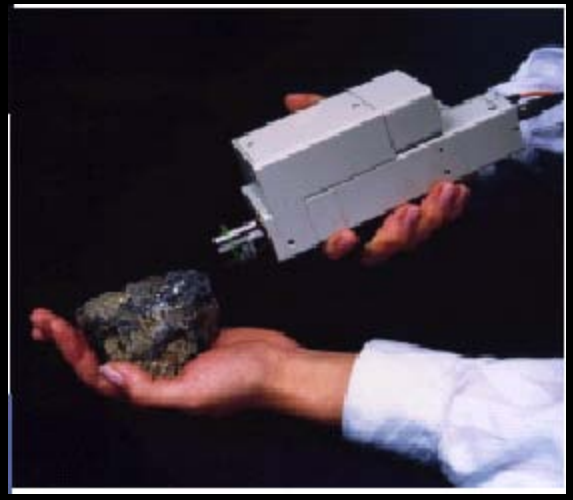




1997 at UVA







2005

The Raman Spectrometer

for Exomars

ExoMars is the first mission in ESA's Aurora Exploration Programme.

Credits :ESA

ExoMars mission's scientific objectives are:

To search for signs of past and present life on Mars;

To characterise the water/geochemical environment as a function of depth in the shallow subsurface;

To study the surface environment and identify hazards to future human missions;

To investigate the planet's subsurface and deep interior to better understand the evolution and habitability of Mars.

A Raman-LIBS instrument was considered as “essential” inside the ExoMars payload. The main scientific objectives are defined in the document “Scientific Payload Requirements” (EXM-PL-RS-ESA-00001)

1) to contribute to the search for biomarkers in support of the mission’s exobiology goals;

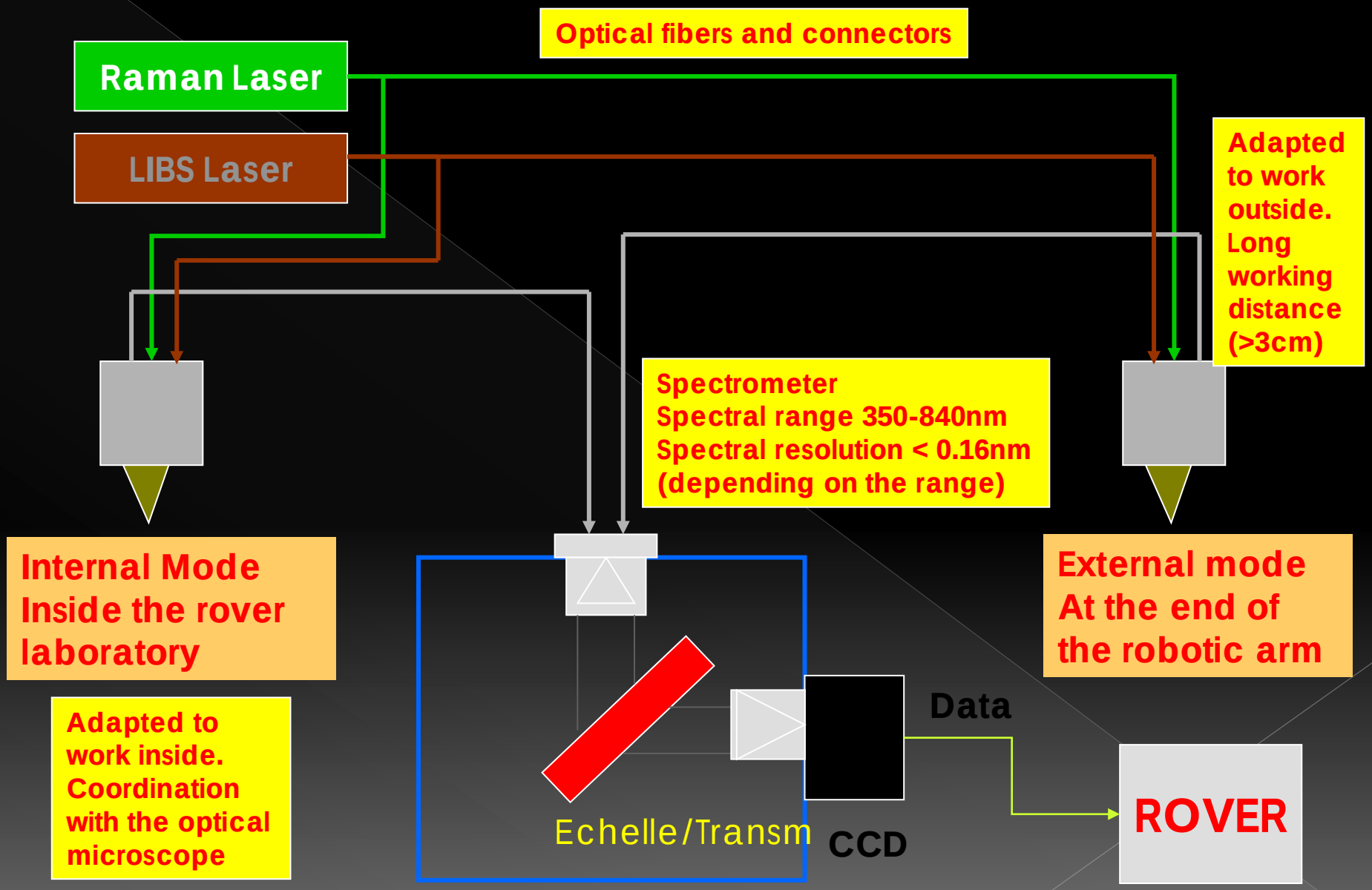
2) to identify mineral products that are indicators of biologic activity;

3) to characterise mineral phases produced by water-related processes;

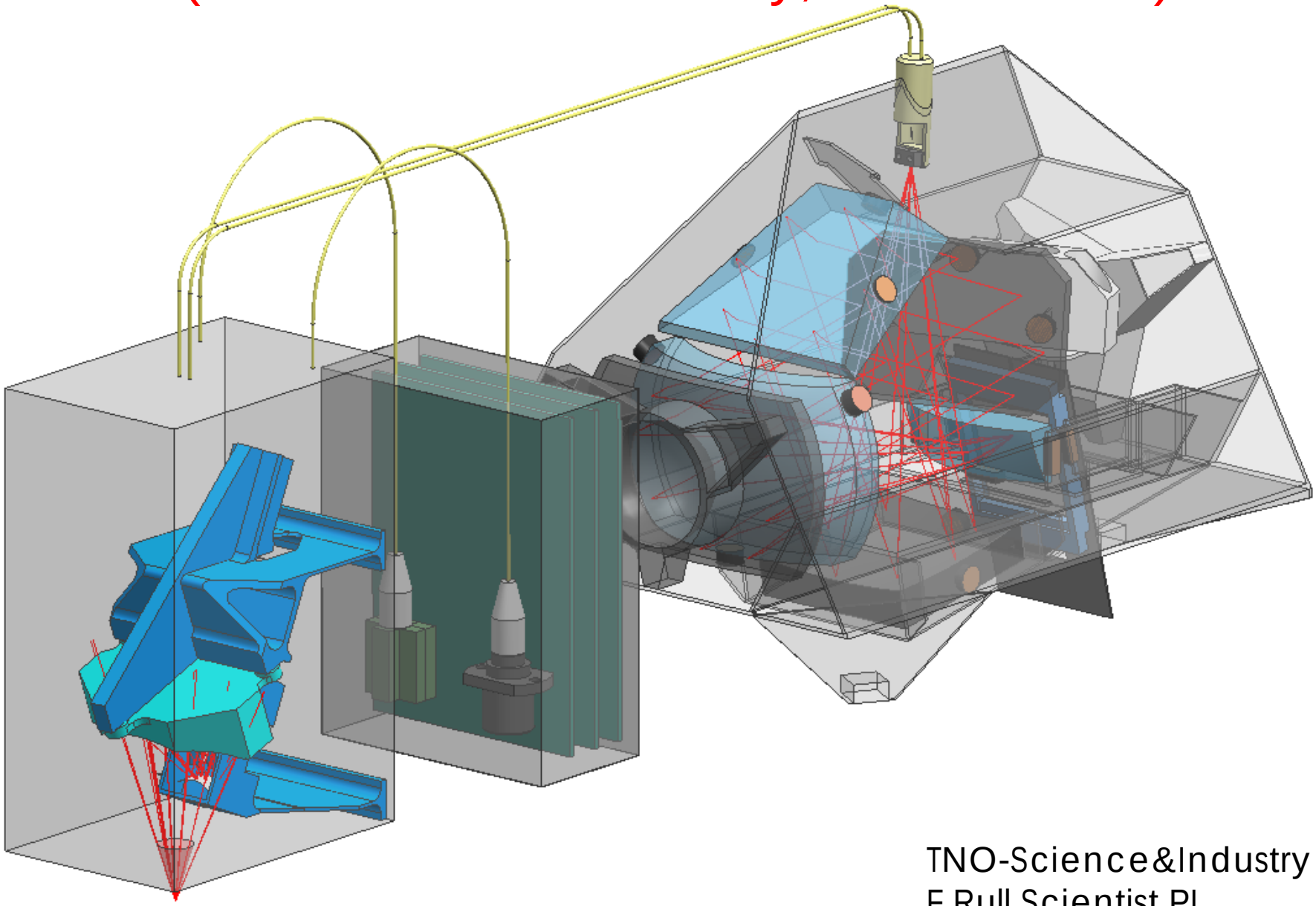
4) to study igneous minerals and their alteration products.

Key: Combination of Petrology, Mineralogy and Geochemistry at the same spot

Raman-LIBS overview

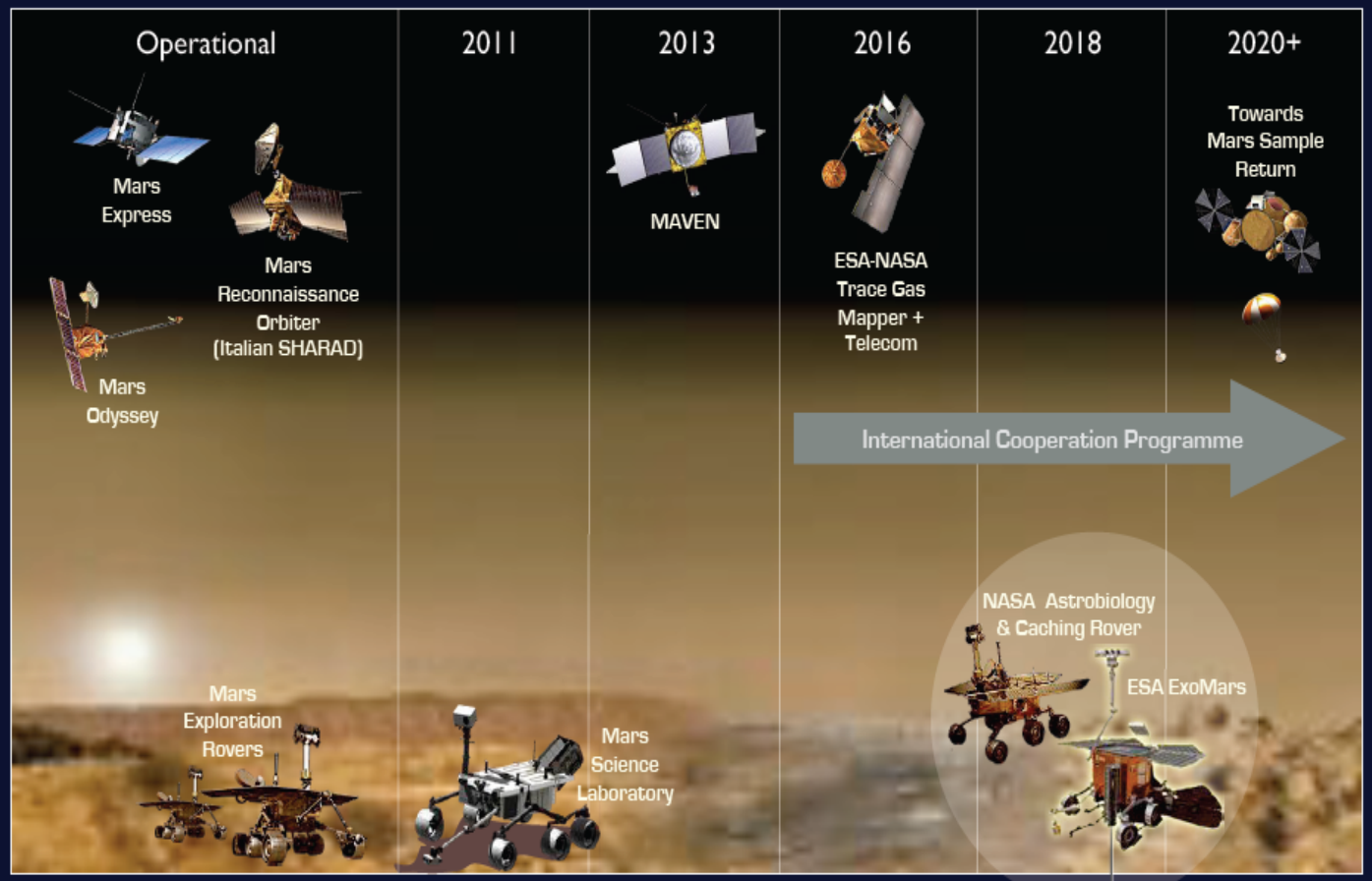


Raman-LIBS EBB
(TNO-Science&Industry, Netherlands)



TNO-Science&Industry
F.Rull Scientist PI

New International Context



- **MSL**: powerful rover; large 2-D mobility.
- **ExoMars**: next-generation instruments; 3-D access.

Following on the results of MSL, ExoMars is the logical next step in international Mars surface exploration.

Instrument Evolution

science

(2002-2003)

- Imaging: ext. & int.
- LIBS: ext. & int.
- Raman: ext. & int.

DREAM instrument

(2005)

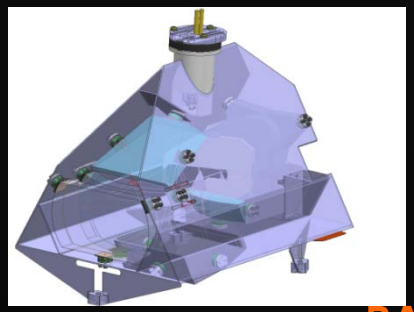
- LIBS: ext. & int.
- Raman: ext. & int.

A & A-1 (240-840nm)

Trade-off Options

BASELINE

EBB



- LIBS: ext.
- Raman: ext. & int.

B (240-840nm)

(2007)

- LIBS: ext. & reduced λ range
- Raman: ext. & int.

C (350-840nm)

C1(535-750nm)

(2007)

BASELINE at SRR

(Mass > 3kg)

(2008)

D (535-670nm)

- Raman: ext. & int.

E (535-670nm)

- Raman: ext.

ESA letter 20/06/2008
Mass limit 2.5kg

PDR instrument

Floor Inst.

PCR#2 May 2009

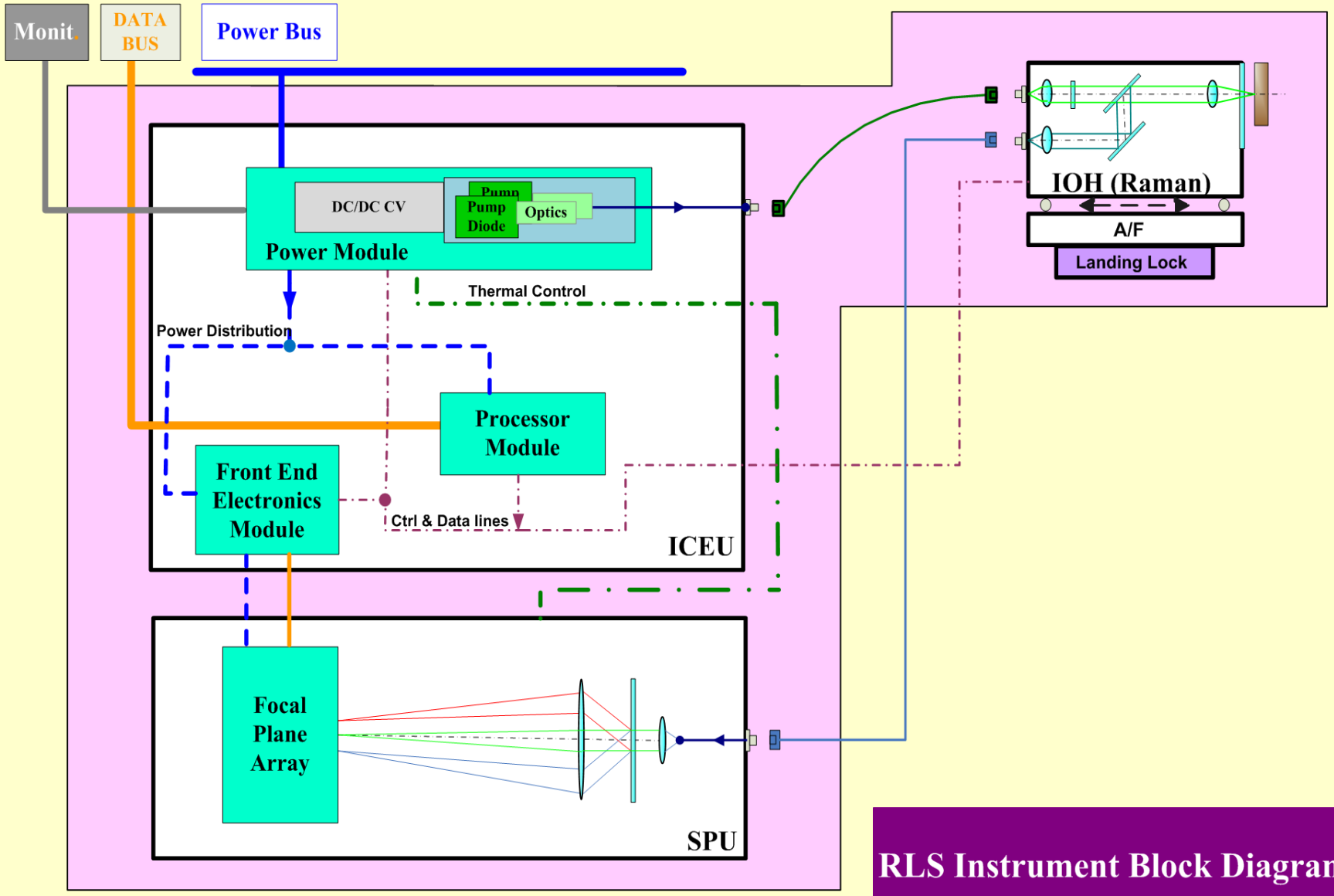
Raman: int.
Powder samples

2011- ESA-NASA??

New operation Mode& new requirements

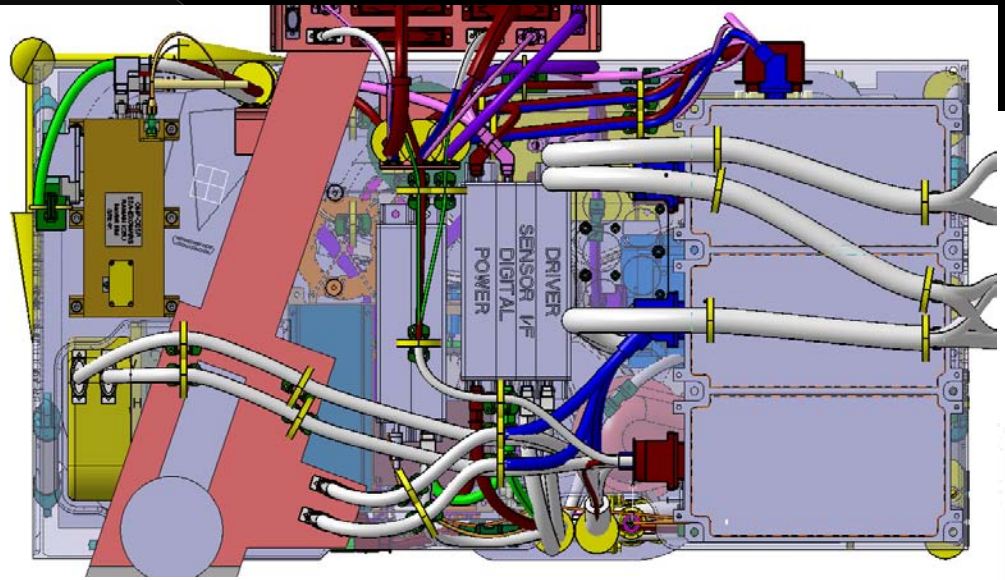
2012-ESA-Roskosmos ??

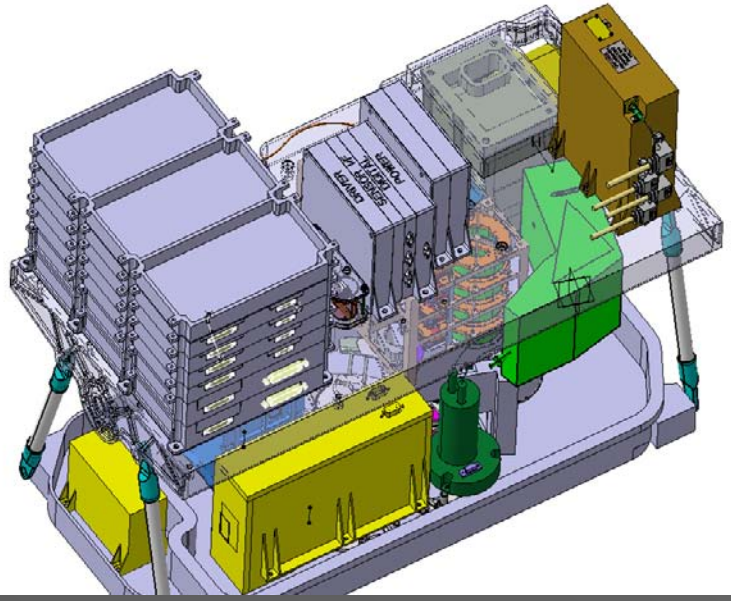
Raman: int.
Powder samples

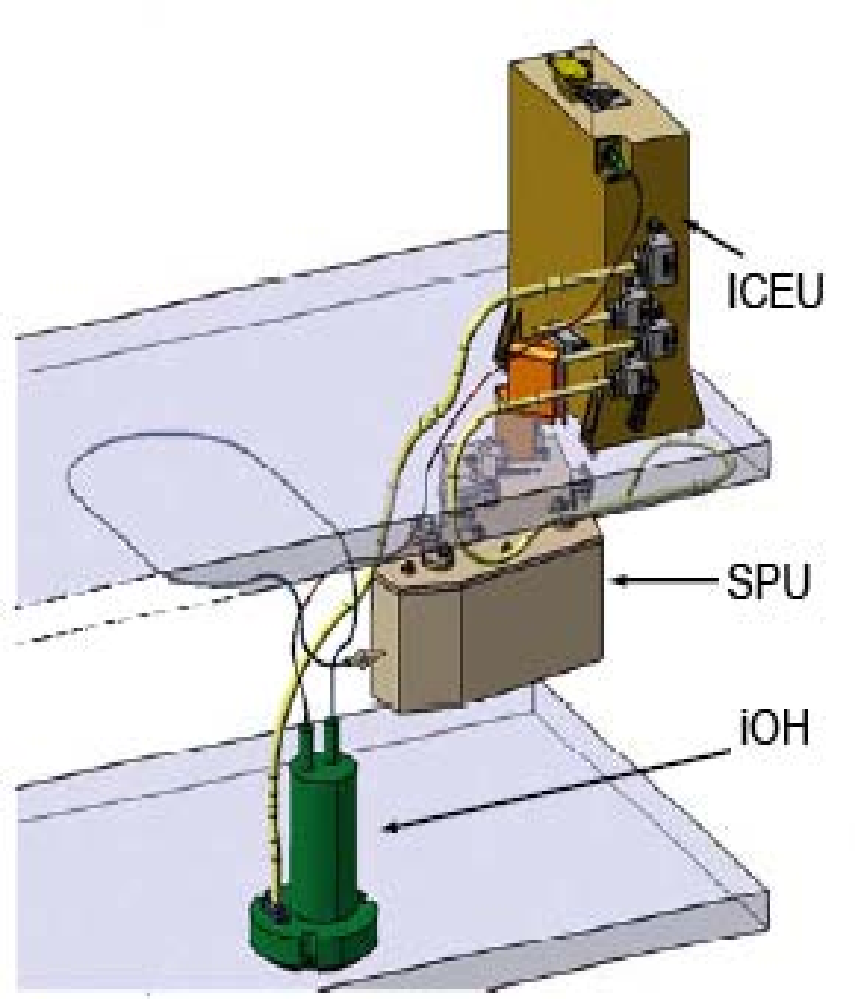


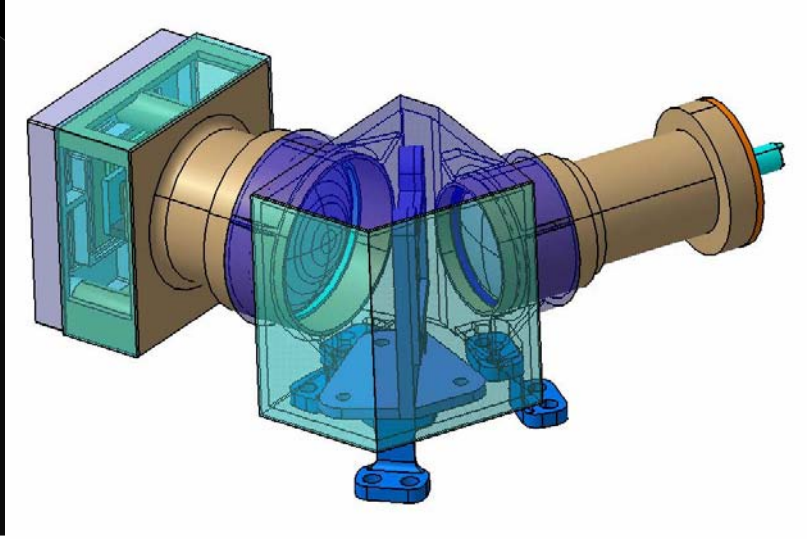
RLS Instrument Block Diagram

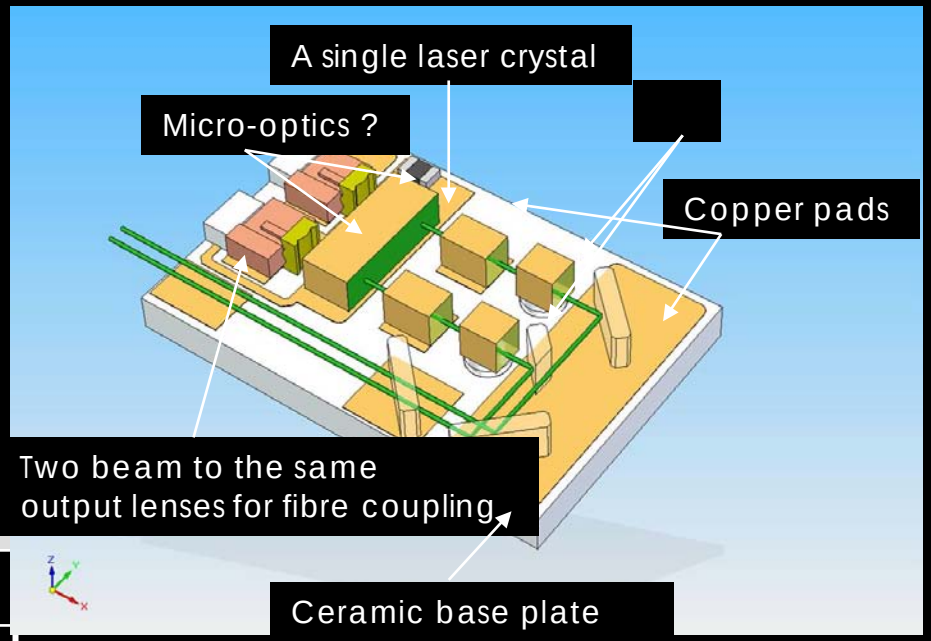
Rover ALD accommodation



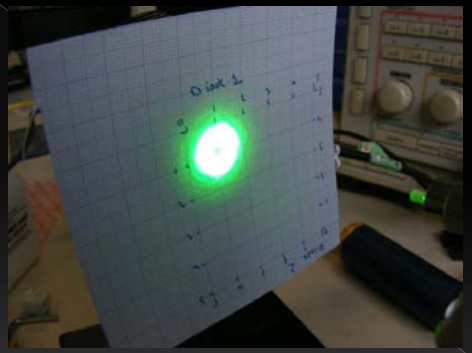




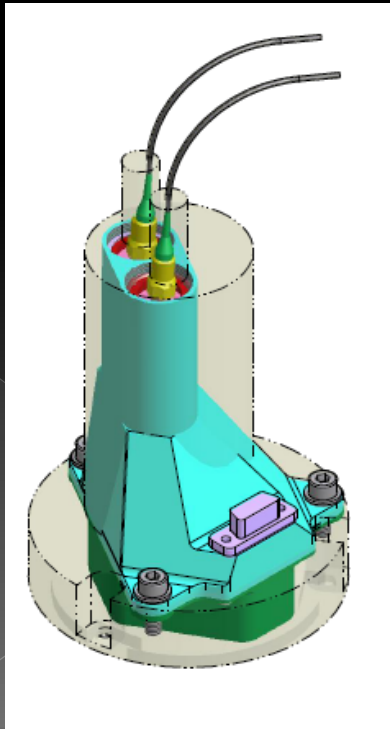


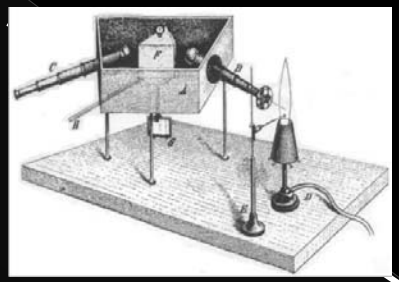


	PM9	M 0.7	Trade-off PM7
Focal Length COLLIMATOR	72.10 mm	69.47 mm	82.13mm
Focal Length COLLECTOR	72.07 mm	48.77 mm	37.17mm
M	1:1	1:1	2:1
AN	0.22	0.22	0.11
OAL fibre-grating	93.27 mm	92.39 mm	95.18 mm
OAL grating-CCD	98.04 mm	82.14 mm	45.99 mm
Weight lens	217.7 gr (without apertures)	189.53 gr	47.12 gr
Pixel size	15µm	15µm	15µm
Extension (pixels)	~1500	~1300	~1000
Resolution	0.09-0.11nm/pixel	0.11-0.14nm/pixel	0.15-0.19nm/pixel
Dispersion	6-7nm/mm	7.7-9.6nm/mm	10-12.6nm/mm
Throughput	0.5 (theoretical)	0.5 (theoretical)	0.223



Current FM configuration

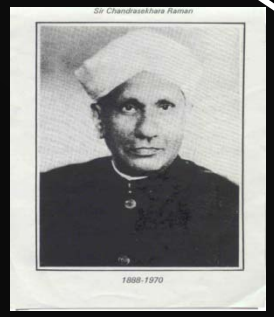




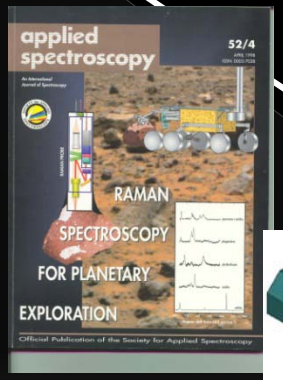
Kirchhoff_Bunsen_1823

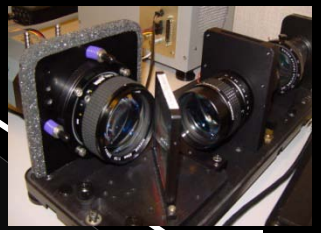
Raman first spectrograph 1928

Raman Spectrum CCl4

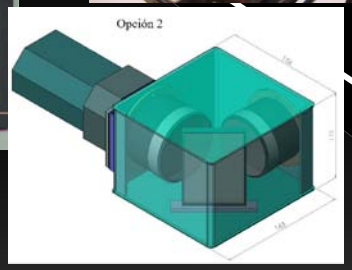


Larry Haskin et al. 1998





Rull-UVA-BB 2003

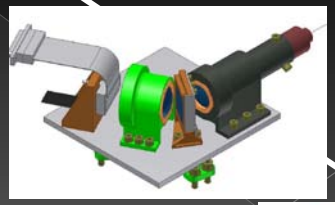


Rull-UVA-BB/NTE 2005

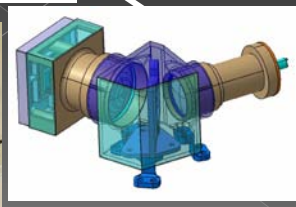
S. Sharma 2008

PM#7 2009

rls-int-tn-006-DraftB



RLS-2011



Rull-UVA-Lidax 2011

Raman Transmission Spectrometer Heritage

RLS Scientific Activities

√ **Science with the operation mode simulator**

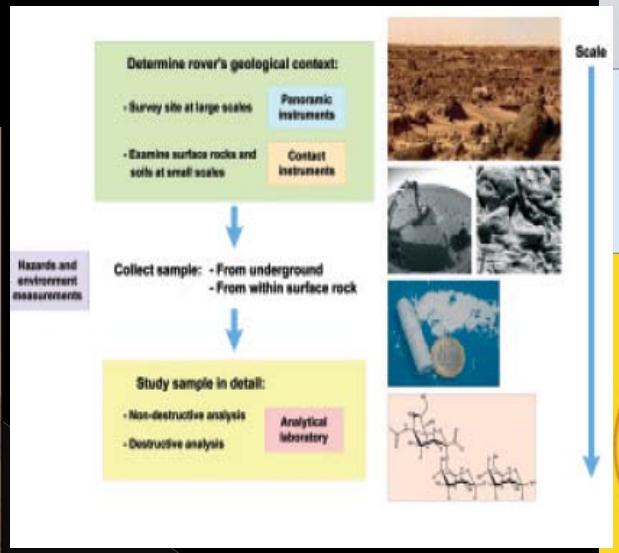
√ **Field activities on potential Martian analogues and sample multidisciplinary analysis (**Rio Tinto; Jaroso; Tenerife; Campo de Calatrava; Iceland; Svalbard (AMASE); Barberton (South Africa); Antarctic, Atacama, others)

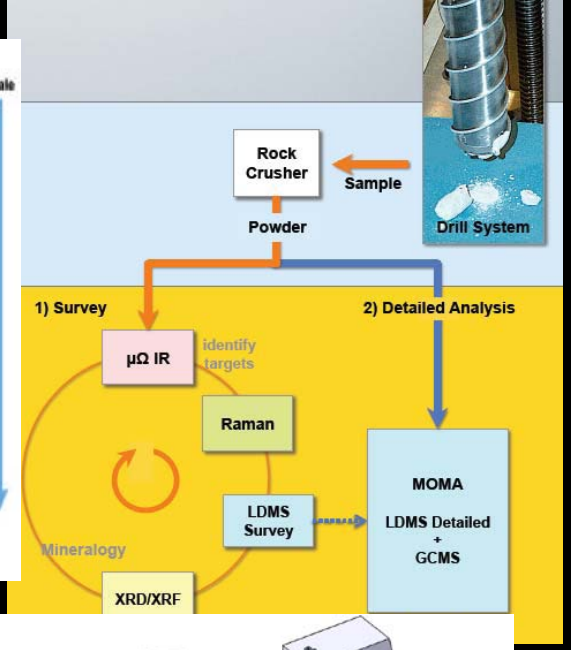
√ **LIBS-Raman geochemical correlations and Raman band-parameter analysis for structural and chemical information from spectra (chemometrics)**

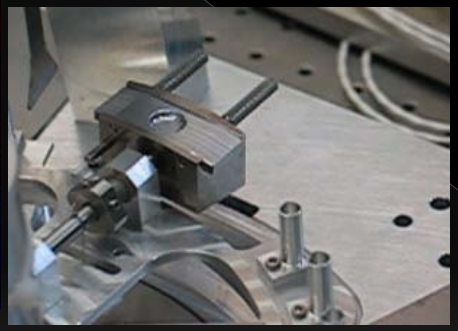
√ **Databases and data management**

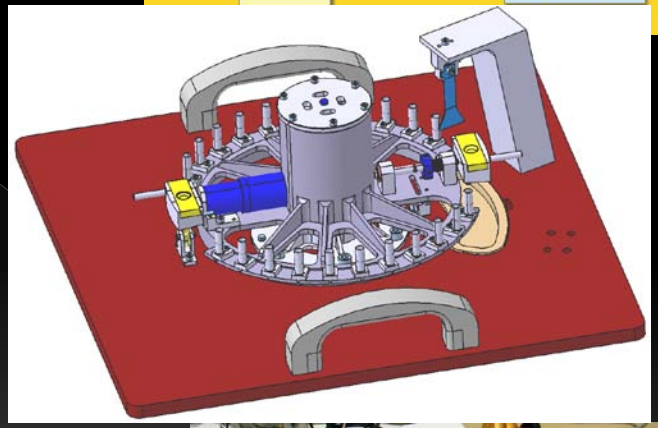
√ **Interaction biology-geology**

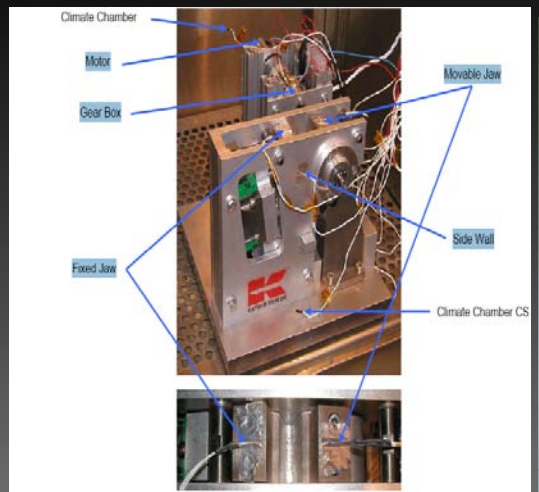
EXOMARS Experimental Cycle

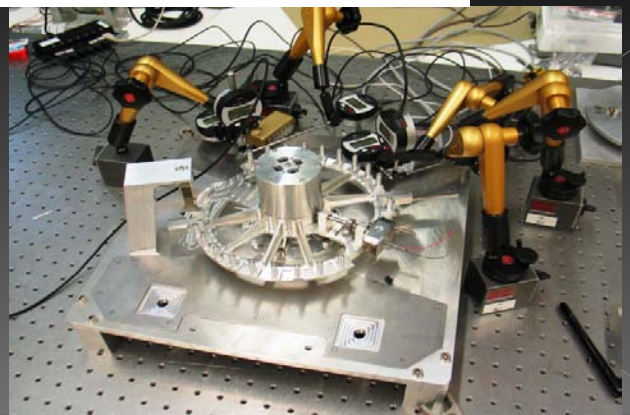












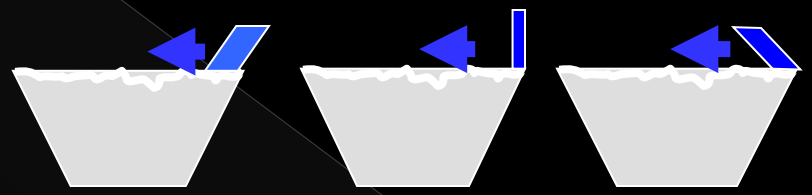
Raman Operation Mode: Internal OH on powdered samples

Powder characteristics are of great importance for the science

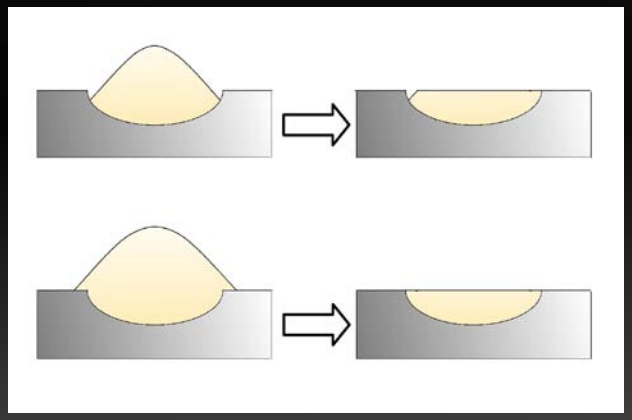
1- Grain size distribution

2- Surface flatness and compaction degree

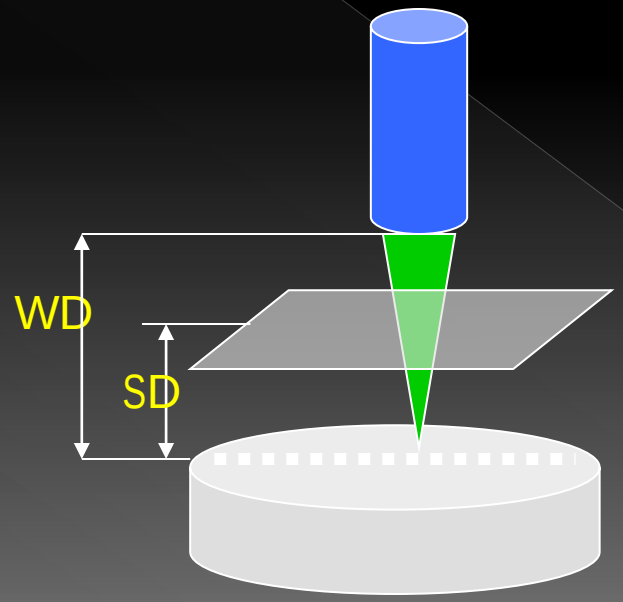
These characteristics depends on the sample nature and the crushing and flattening method



Flattening possibilities



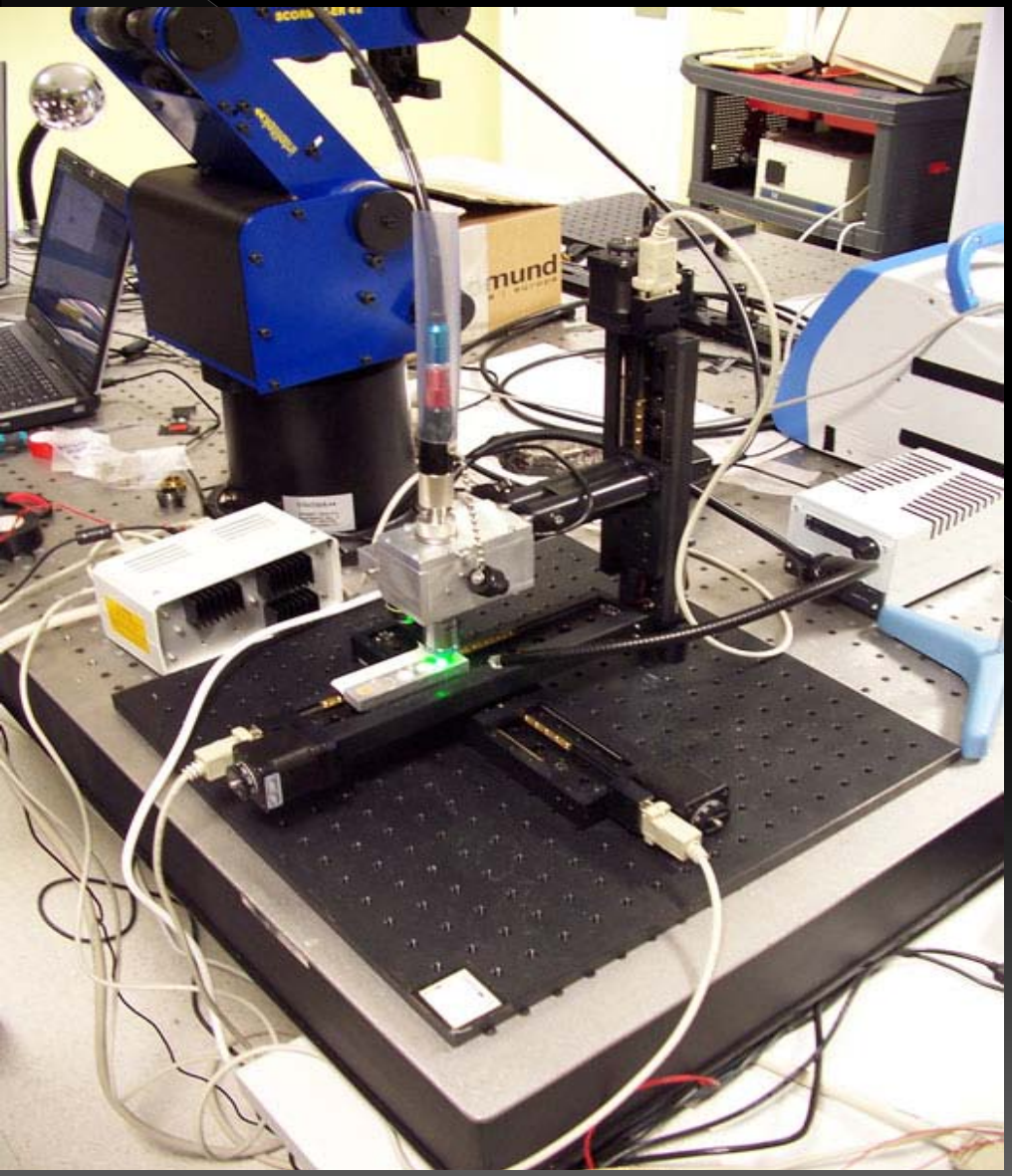
Different ways for powder distribution and dosing

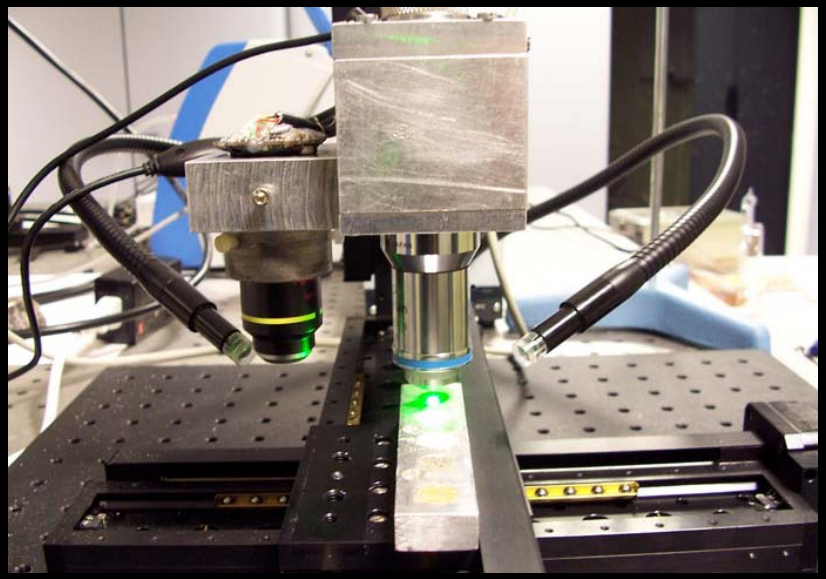


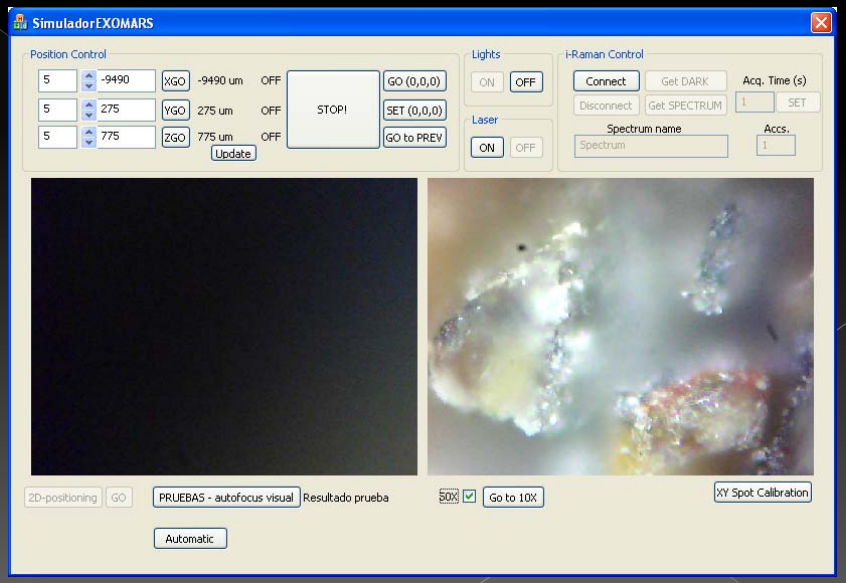
Driving parameters

WD: Working Distance
SD: Safe Distance
SP: Spot Diameter
DoF: Depth of field

Powder analysis simulator developed at the Unidad Asociada UVA-CSIC-CAB

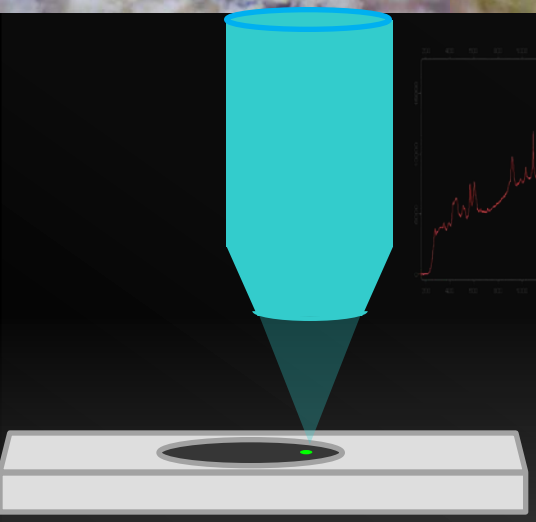


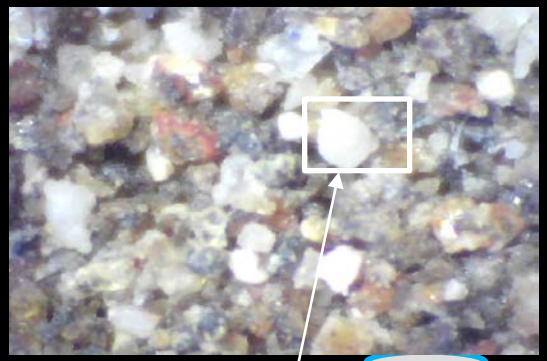


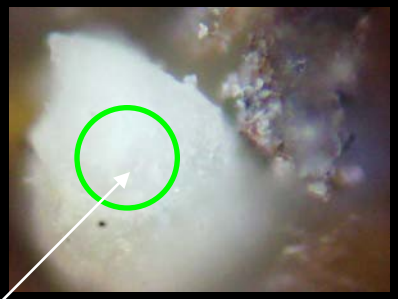


•**Simulator General Description**

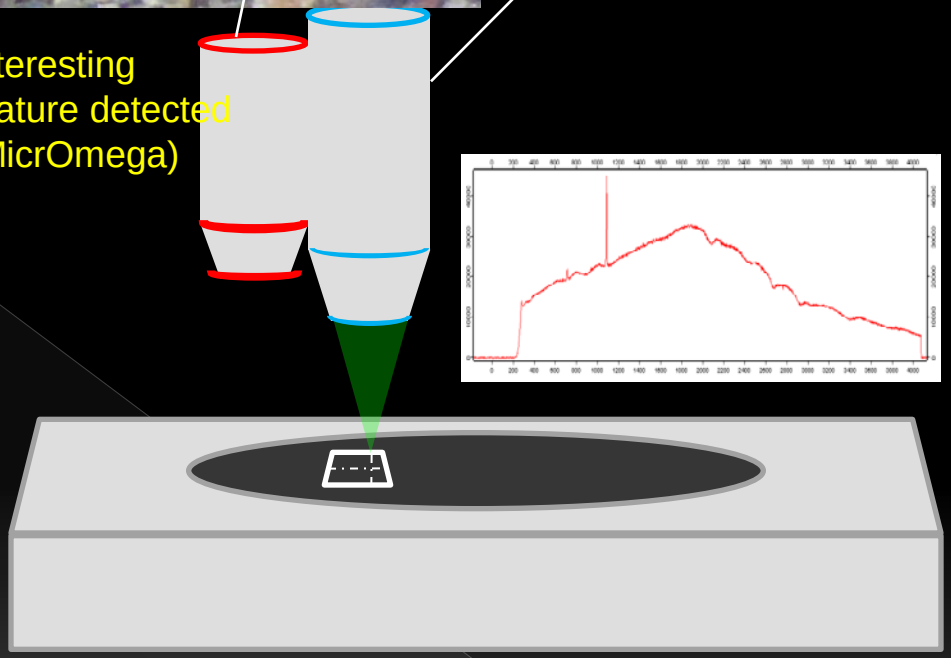
- XYZ positioners. 2.5µm resolution
- Two cameras and objectives with a beamsplitter
- Illumination system
- Transmission Spectrometer and 532 nm laser
- Raman iOH





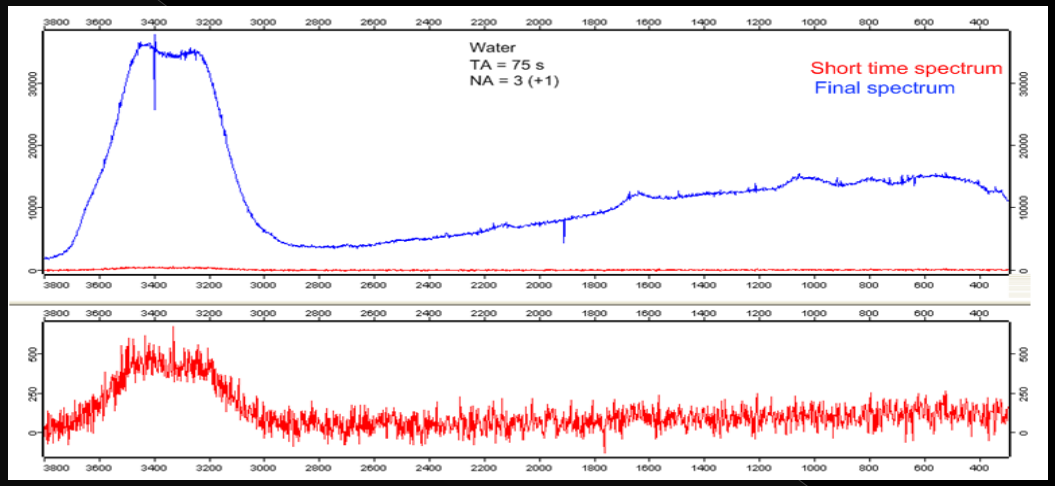


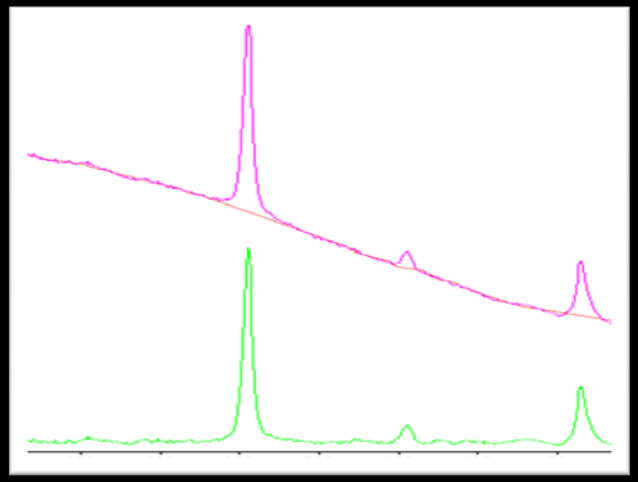
Interesting feature detected (MicrOmega)



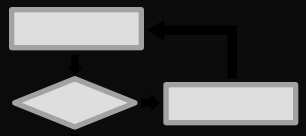
- **1D sampling: along one line**
- **2D mapping:**
- **Smart Collaborative science in coordination with other instruments**

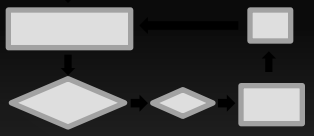
RLS operation mode algorithms





Identification of cosmic rays and saturation by fluorescence

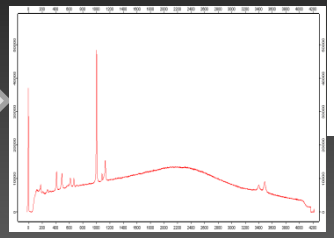


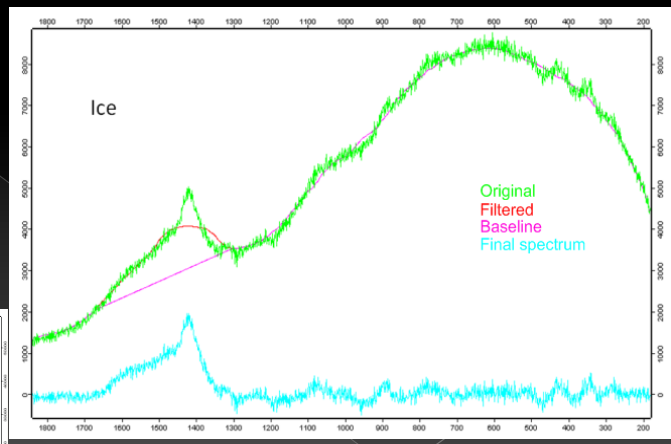


Identification and reduction of fluorescence

Adjustment of the acquisition parameters

Acquisition



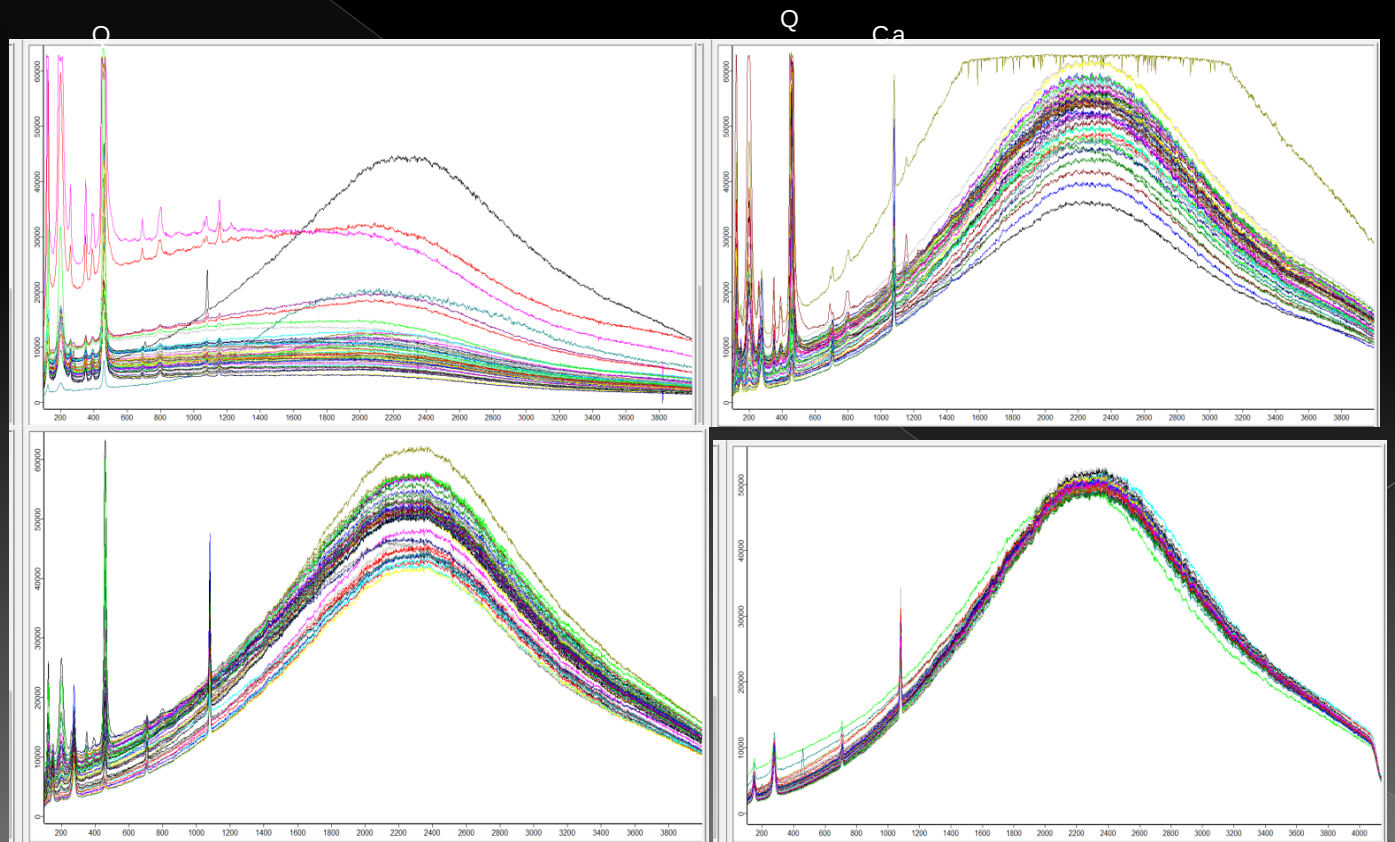


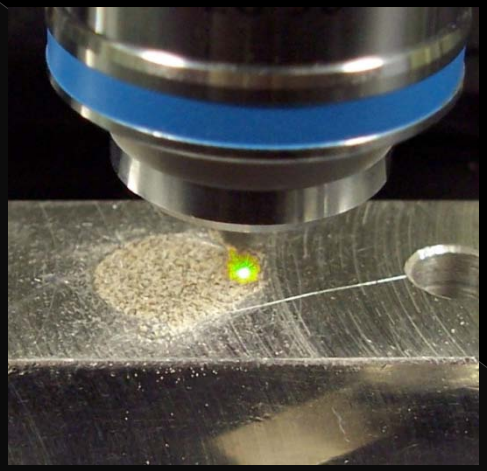
Results

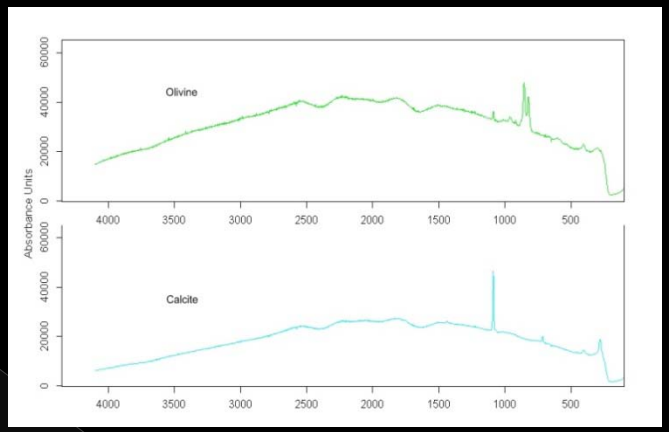
Analysis of mixtures of different powdered minerals has been performed to asses the capability of the instrument to identify and quantify individual mineral phases. Mixtures ranged from 1-99% and the spectral analysis was performed from 5 parallel lines of 30 point each (i.e. 150 spectra per sample). Intensity of each compound was calculated as the integrated area of all the detectable bands assigned to this compound.

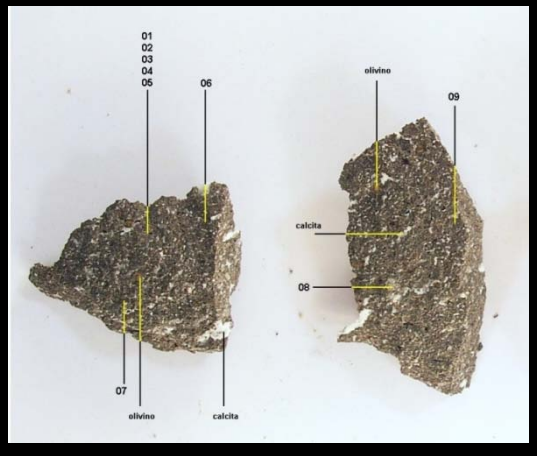
Spectra were obtained automatically by the simulator at regular intervals.

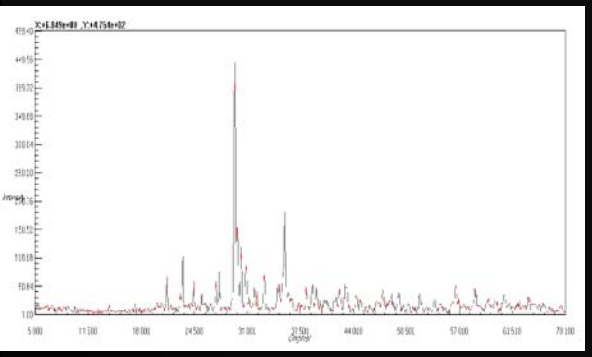
Acquisition parameteres were also automatically obtained. Raw data without spectral corrections is depicted.

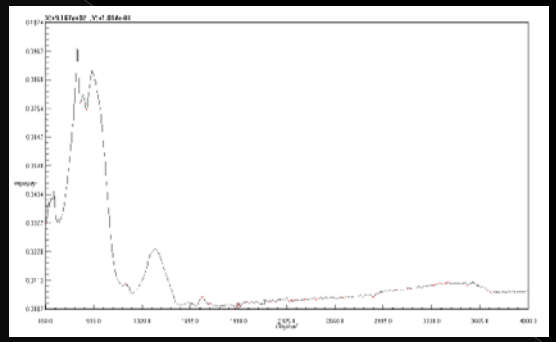


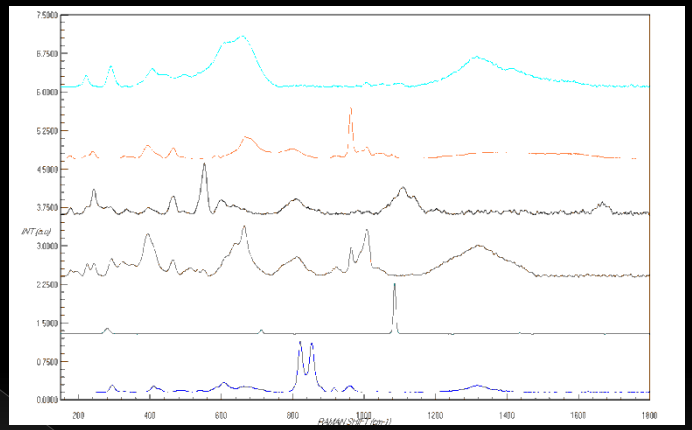








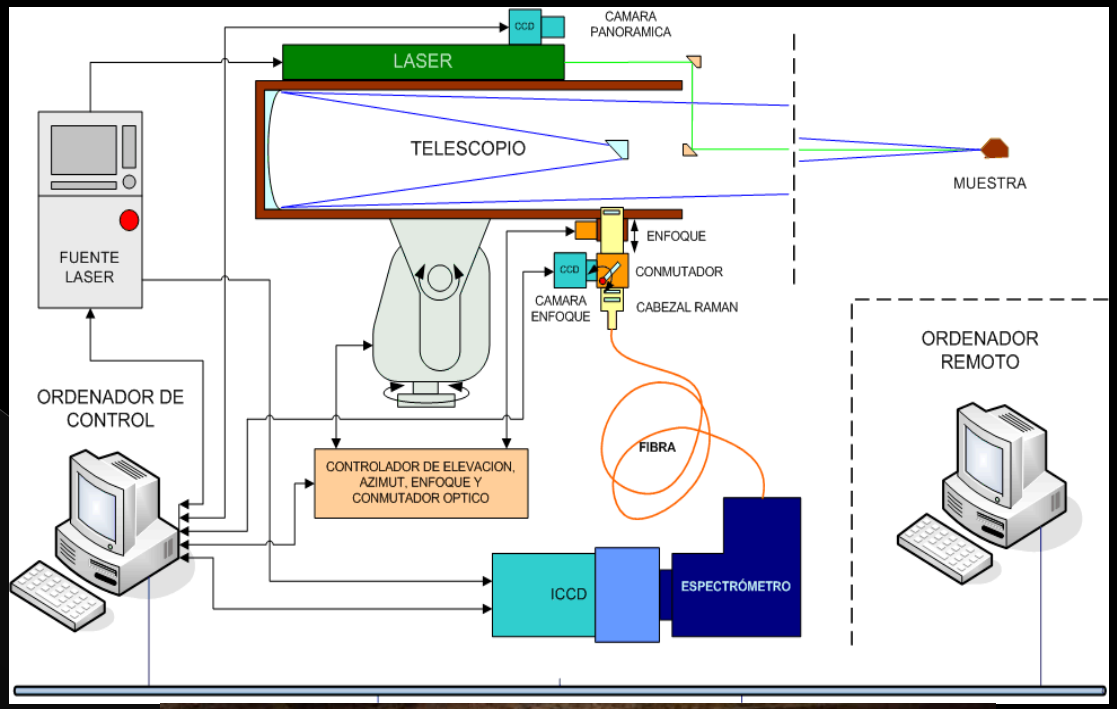




III-Altered basalt (Calatrava, SP)

Technique	Pyroxenes	Olivine	Nepheline	Sodalite	Calcite	Hematite
Raman on solid	✓	✓	✓?	✗	✓	✓
Raman on powder	✓?	✓	✓?	✓?	✓	✗
DRX	✓	✓	✓	✓	✓	✗
ATR	✗	✓	✗	✗	✓	✗

Science Simulators for field applications

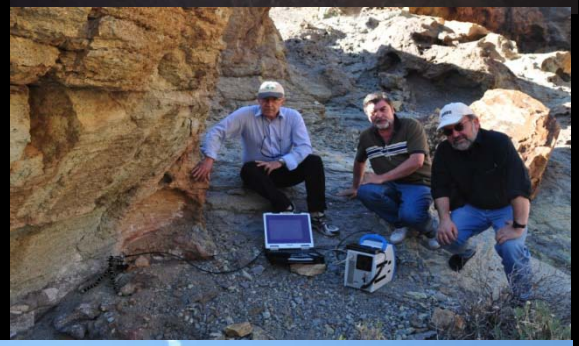


Rio Tinto

Svalbard (AMASE)

Tenerife

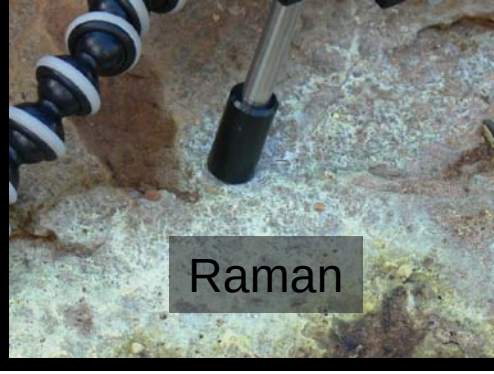
JPL

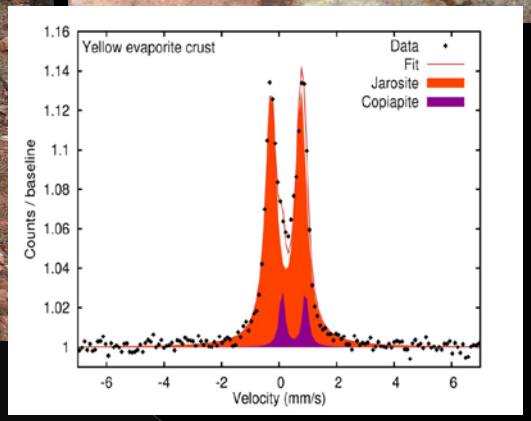


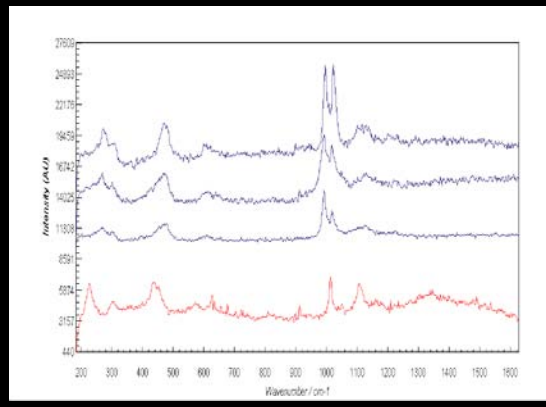
Jaroso

Mauritania

Barberton

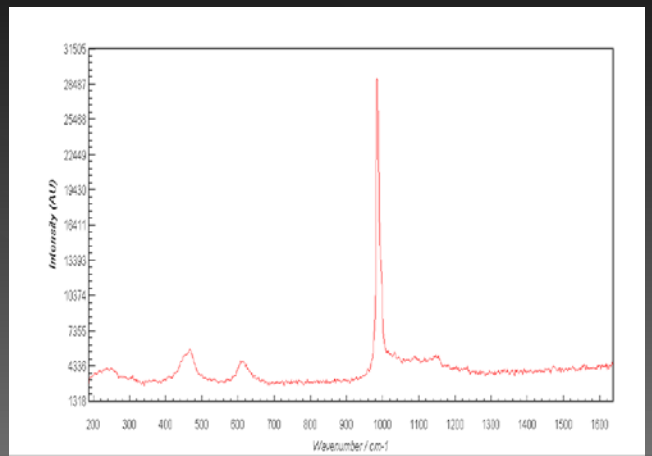


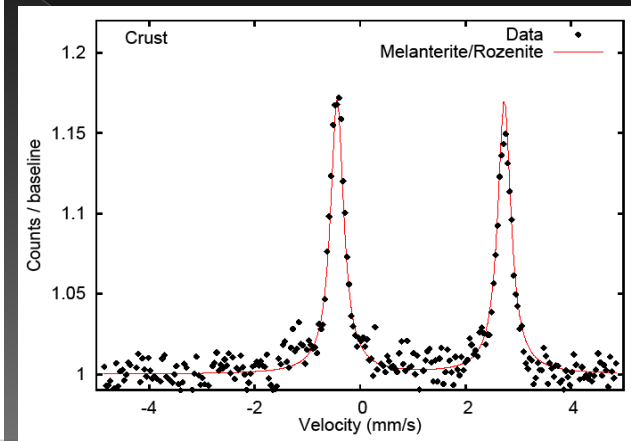


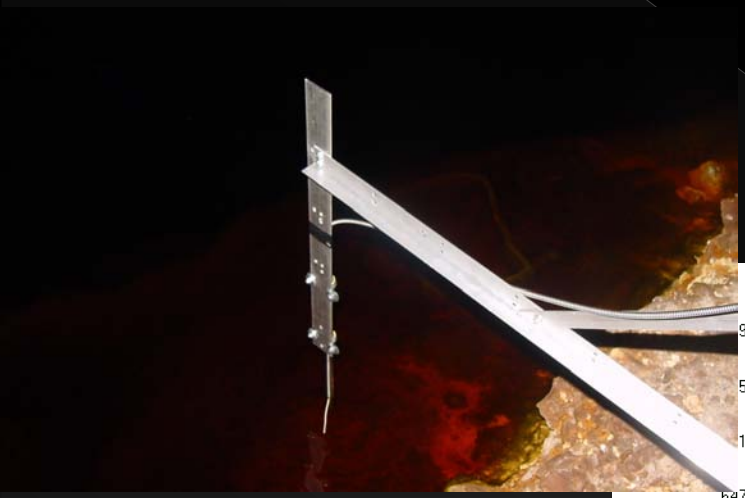


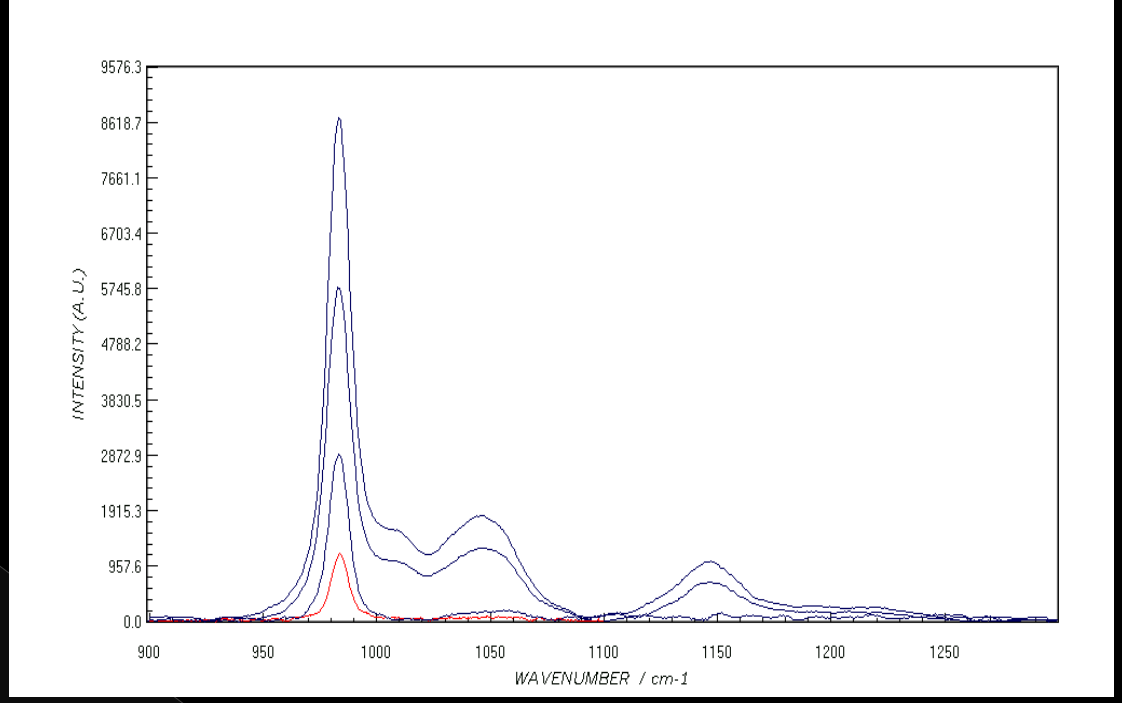
External operation mode at Rio Tinto Coordination with Moessbauer (June 2008)

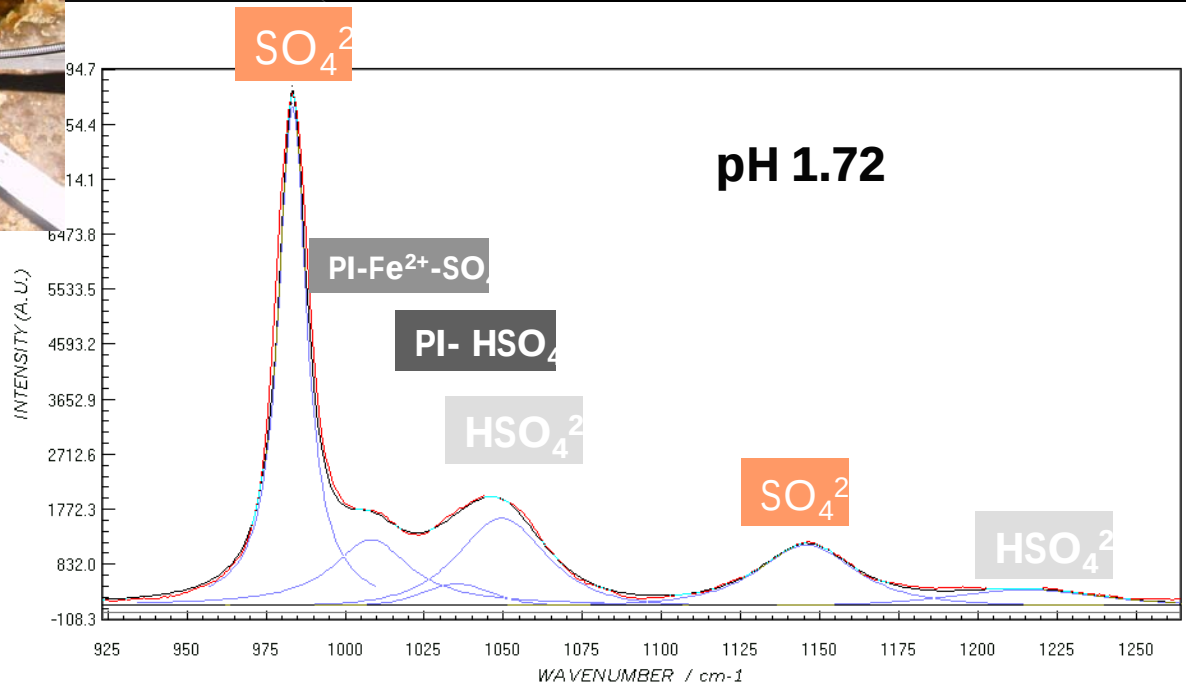
Top: copiapite with different structural order, Bottom: jarosite at some yellow spots.





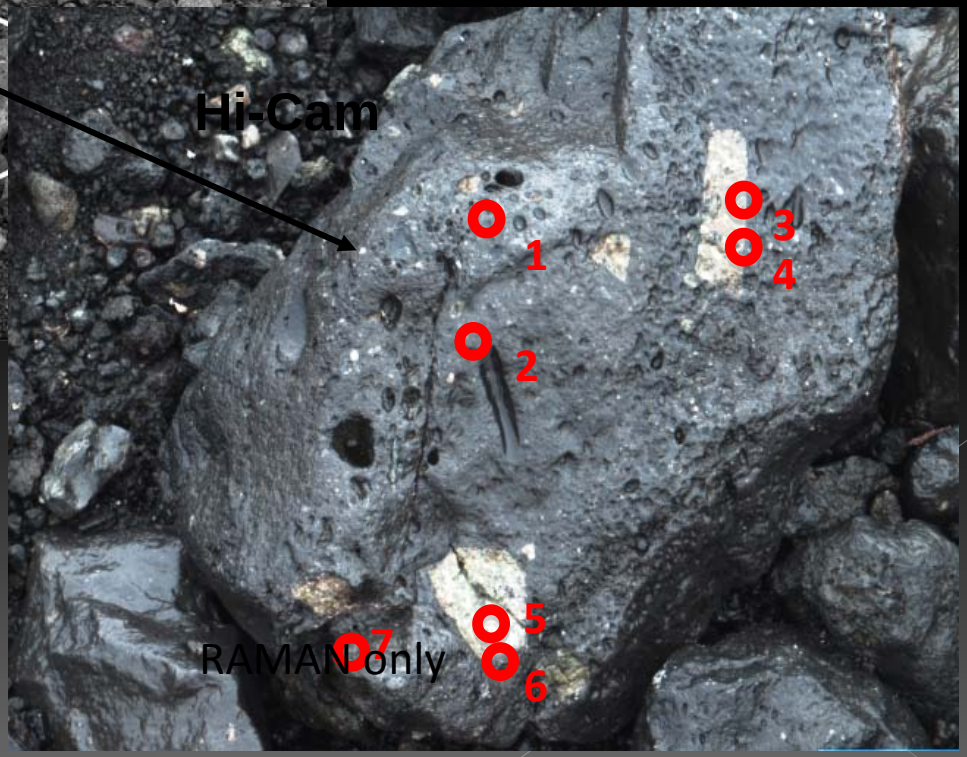



9576.3
8618.7
7661.1
6703.4
5745.8
4788.2
3830.5
2872.9
1915.3
957.6
0.0
INTENSITY (A.U.)
900
950
1000
1050
1100
1150
1200
1250
WAVENUMBER / cm-1

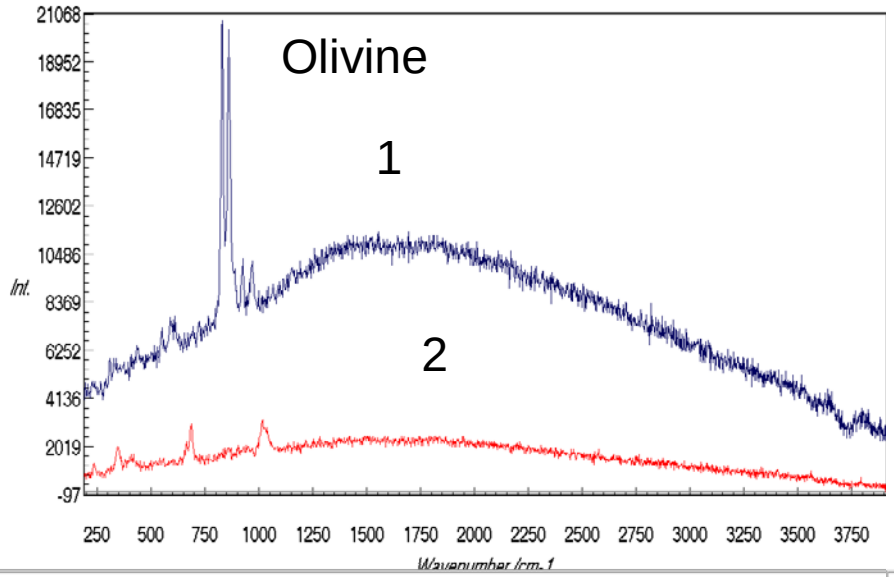

SO_4^{2}
pH 1.72
PI-Fe^{2+}-SO_4
PI- HSO_4
HSO_4^{2}
SO_4^{2}
HSO_4^{2}
5533.5
4593.2
3652.9
2712.6
1772.3
832.0
-108.3
INTENSITY (A.U.)
925
950
975
1000
1025
1050
1075
1100
1125
1150
1175
1200
1225
1250
WAVENUMBER / cm-1

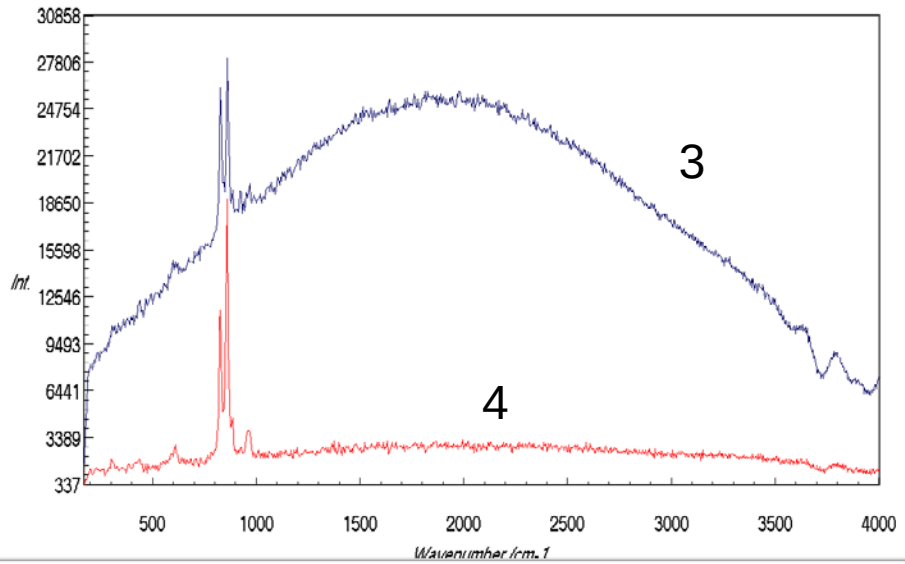
AMASE

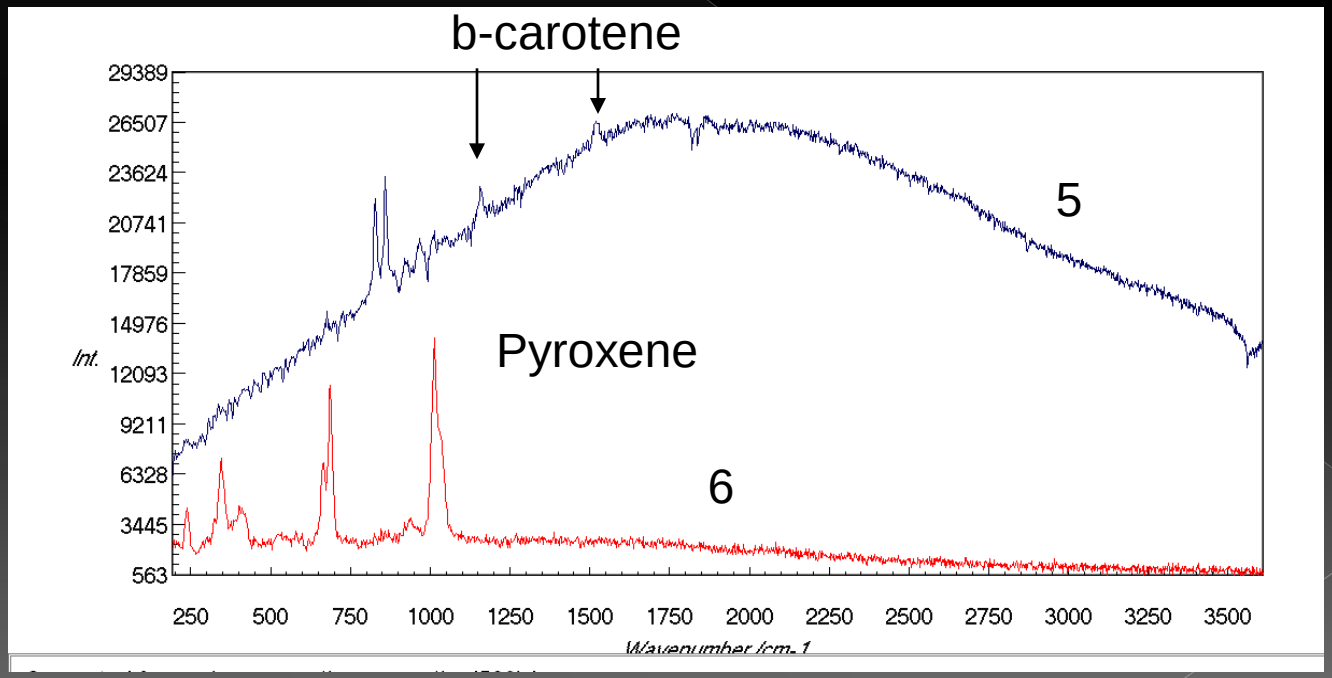
RAMAN PECTROSCOPY IN THE CONTEXT OF THE EXOMARS INSTRUMENT PAYLOAD



PANCAM view of the area with SOWG selected targets encircled and detail of High resolution image of “Plum cake” target showing the different spots requested for contact instrument analysis (Raman) (Credits AMASE 2008)


Olivine
1
2
Int.
21068
18952
16835
14719
12602
10486
8369
6252
4136
2019
-97
250 500 750 1000 1250 1500 1750 2000 2250 2500 2750 3000 3250 3500 3750
Wavenumber /cm-1


3
4
Int.
30858
27806
24754
21702
18650
15598
12546
9493
6441
3389
337
500 1000 1500 2000 2500 3000 3500 4000
Wavenumber /cm-1


b-carotene
5
Pyroxene
6
Int.
29389
26507
23624
20741
17859
14976
12093
9211
6328
3445
563
250 500 750 1000 1250 1500 1750 2000 2250 2500 2750 3000 3250 3500
Wavenumber /cm-1

Thanks for your attention