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Title: The ChemCam Laser-Induced Breakdown Spectroscopy
(LIBS) Instrument on the Mars Rover Curiosity

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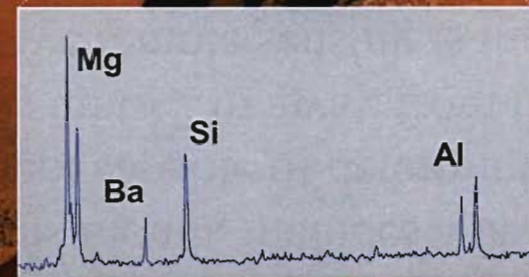
Intended for: Seminar at Delaware State University, Dover
November 15, 2011



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The ChemCam Laser-Induced Breakdown Spectroscopy (LIBS) Instrument on the Mars Rover Curiosity

Roger C. Wiens
Los Alamos
National Laboratory



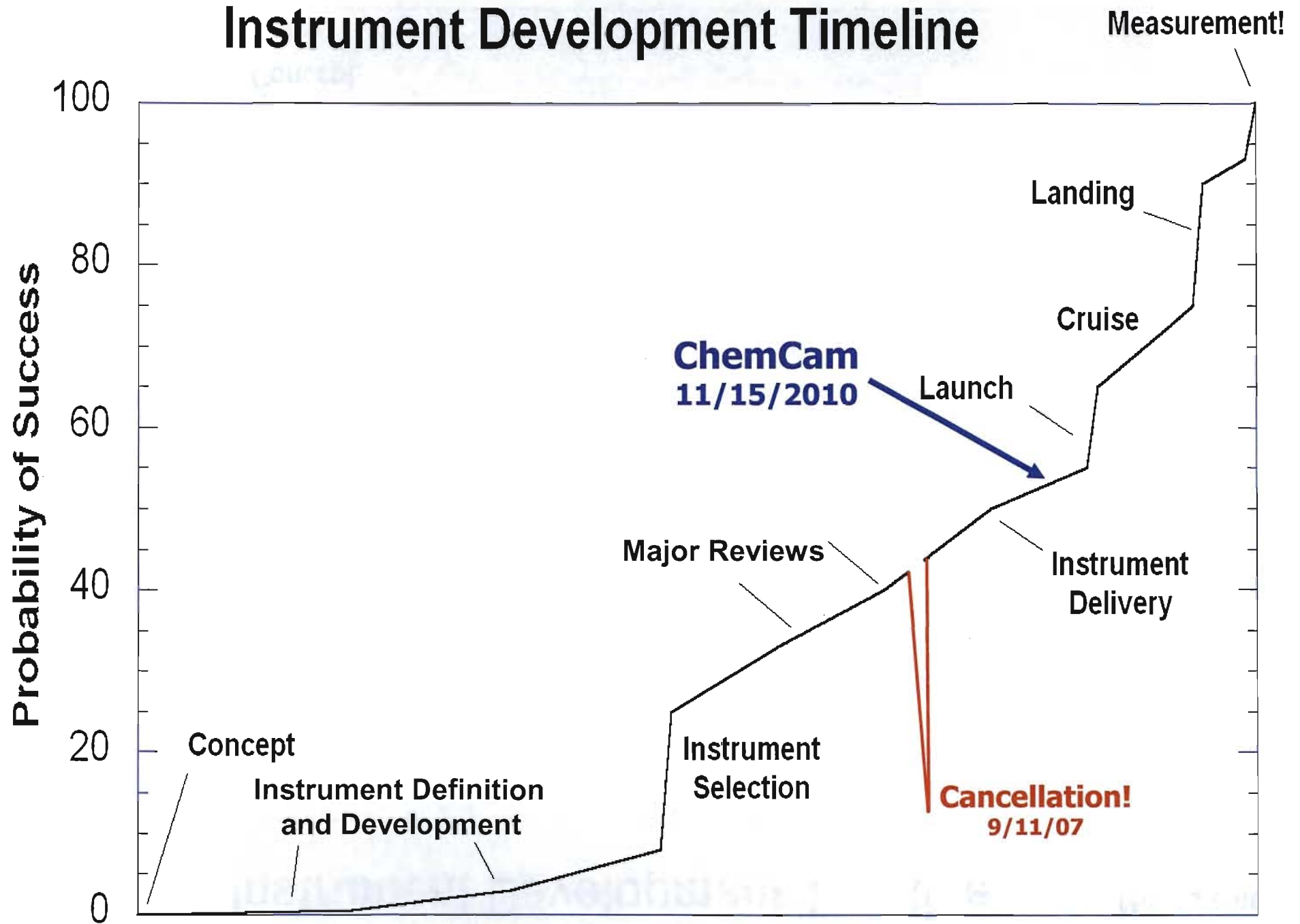
Delaware State University
November 15 2011



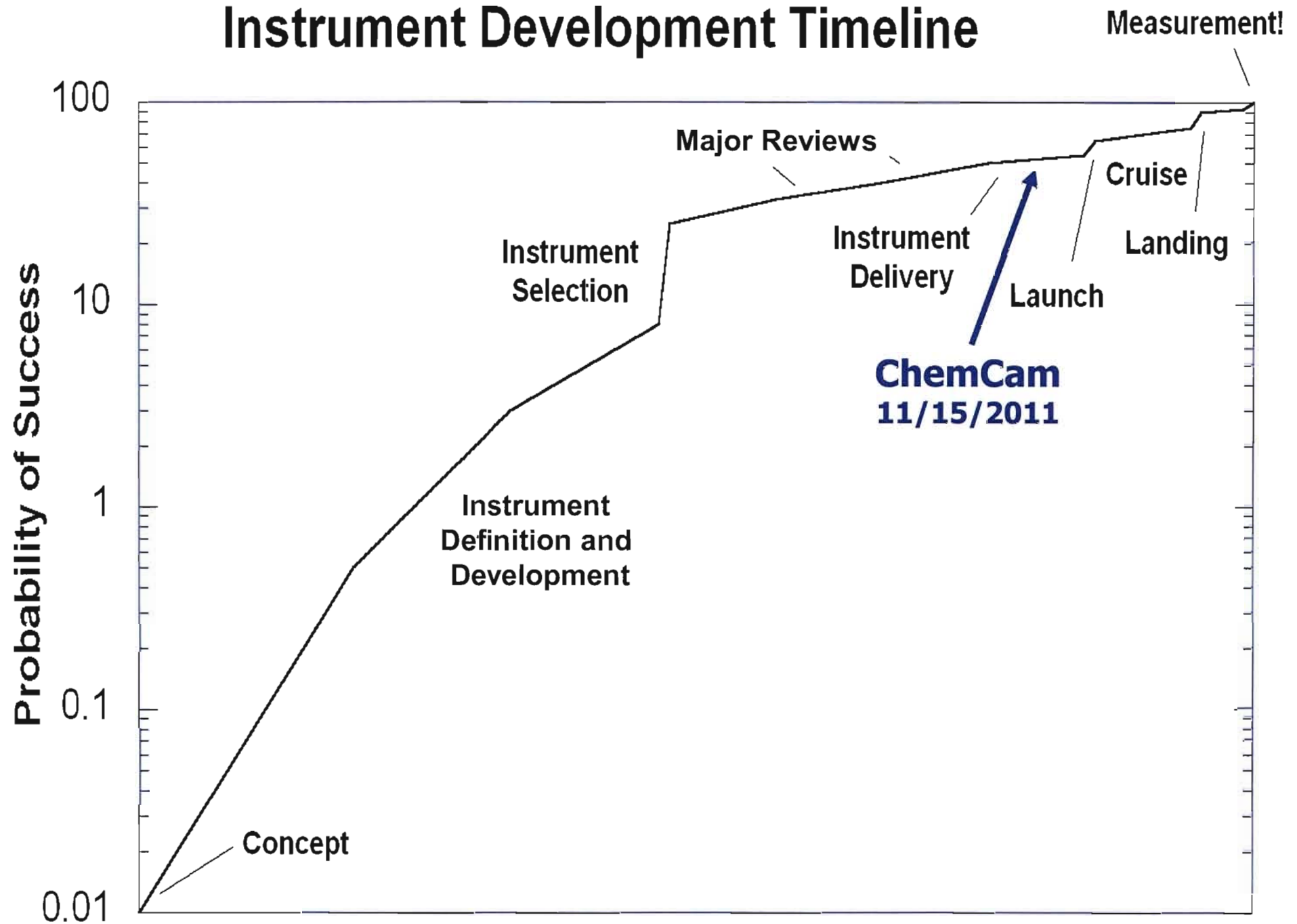
Abstract

- NASA's newest Mars rover, launching this month, includes a laser-induced breakdown spectroscopy (LIBS) instrument capable of determining the elemental compositions of rocks and soils up to 7 m away from the vehicle. A significant advantage for LIBS over passive remote sensing is the ability to remove obscuring dust using repeated laser pulses. Similarly, LIBS can study weathering layers on rocks as well as ablate through to analyze the underlying material. Detecting nearly all elements, ChemCam LIBS will provide the first information on light elements, H, Li, Be, B, C, N, and O, for which the previous Mars rovers lacked the analytical capability. These elements are particularly important in the study of Mars habitability—the goal of this mission—allowing the study of clay minerals and searching for nitrates and carbonates for the first time. I will present the goals of this venture and capabilities of the instrument, highlight the challenges of building the first LIBS device for Mars, discuss LIBS data processing techniques, and outline our operation plans.

Instrument Development Timeline



Instrument Development Timeline



Collaborators

- Dr. Sam Clegg
 - Director of LIBS lab at LANL
 - Instrument Lead for Venus project
- Dr. Jeremie Lasue
 - Postdoctoral Researcher at LANL
 - Expert in Statistical Analysis
- Dr. Sylvestre Maurice
 - ChemCam Deputy PI, Lead in France

Outline

- What is LIBS?
- Why is LIBS needed on Mars?
- Instrument Requirements
- ChemCam
- Data and Operations
- Future applications
 - Venus Lander
 - Lunar & Asteroidal Environments

Why LIBS on Mars?



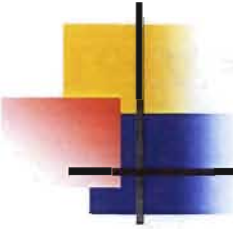
- Mars is a Difficult Place For Remote Sensing
 - Surfaces Typically Covered by Dust and/or Weathering Coatings
 - Active Remote Sensing Much Better Than Passive Under These Circumstances
 - Eagle Crater Sedimentary Rocks Not Initially Identified by Remote Sensing on the Opportunity Rover
 - Most Samples Had to Be Brushed Off Before Identification





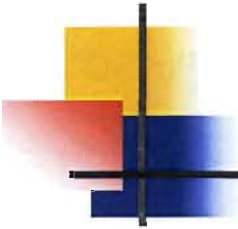
LIBS Advantages

- No sample preparation required
- Rapid analysis technique
- Operates at a distance (ChemCam: 1.5-7 m)
- Removes dust from surfaces
- Provides depth profiles
- Detects nearly all elements
 - Includes H, Li, Be, B, C, N, O
 - Low detection limits for some elements
- Laser requires relatively little power



Top-Level Instrument Requirements

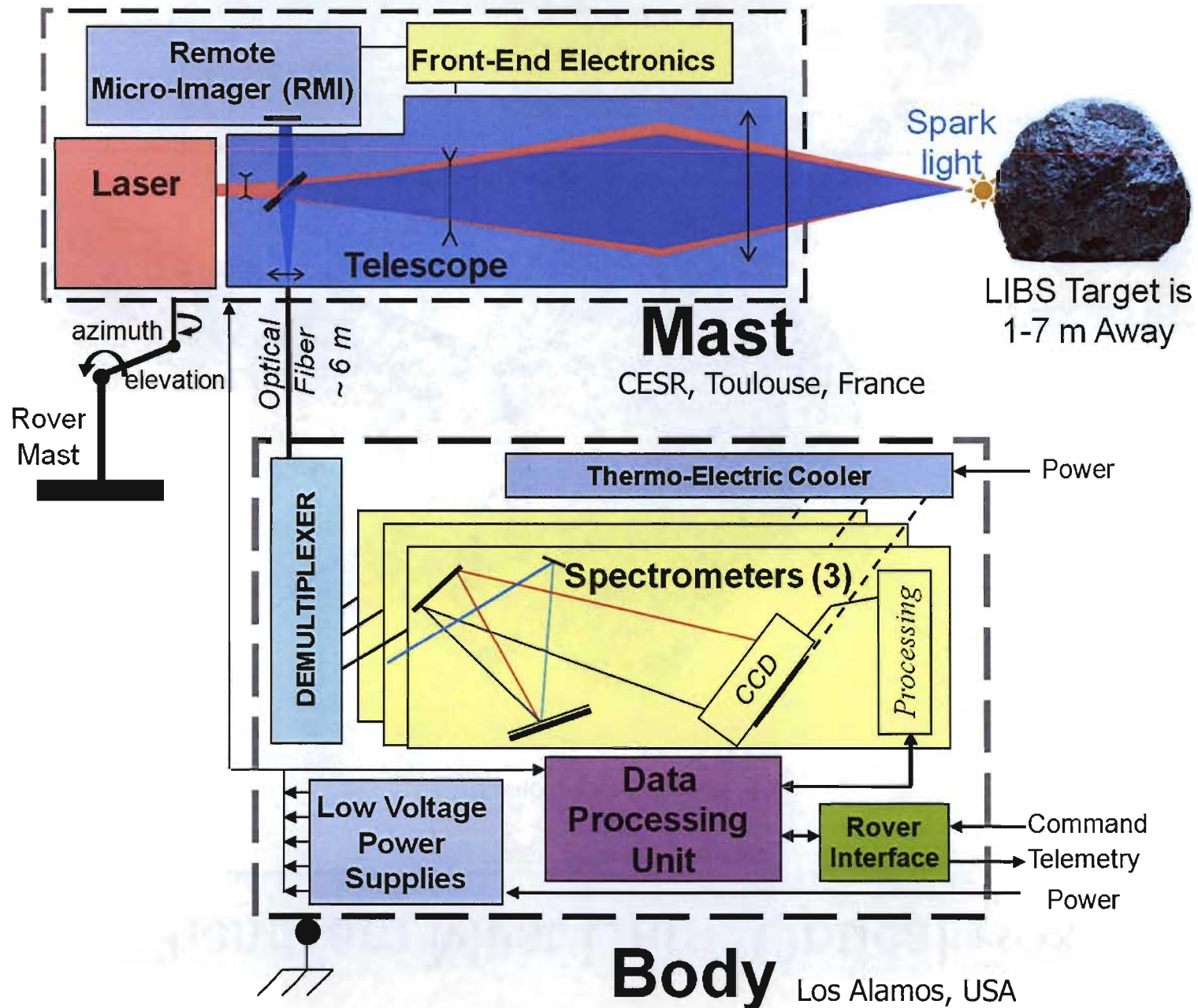
- Measure major elements to $\pm 10\%$ accuracy
- Analysis distances to 7 m
- Capable of up to 10 measurements/day
- Provide depth profiles to 1 mm deep
- Individual shot analyses
- Provide context images for analyses
- Provide rapid analyses (goal 5 min./analysis)



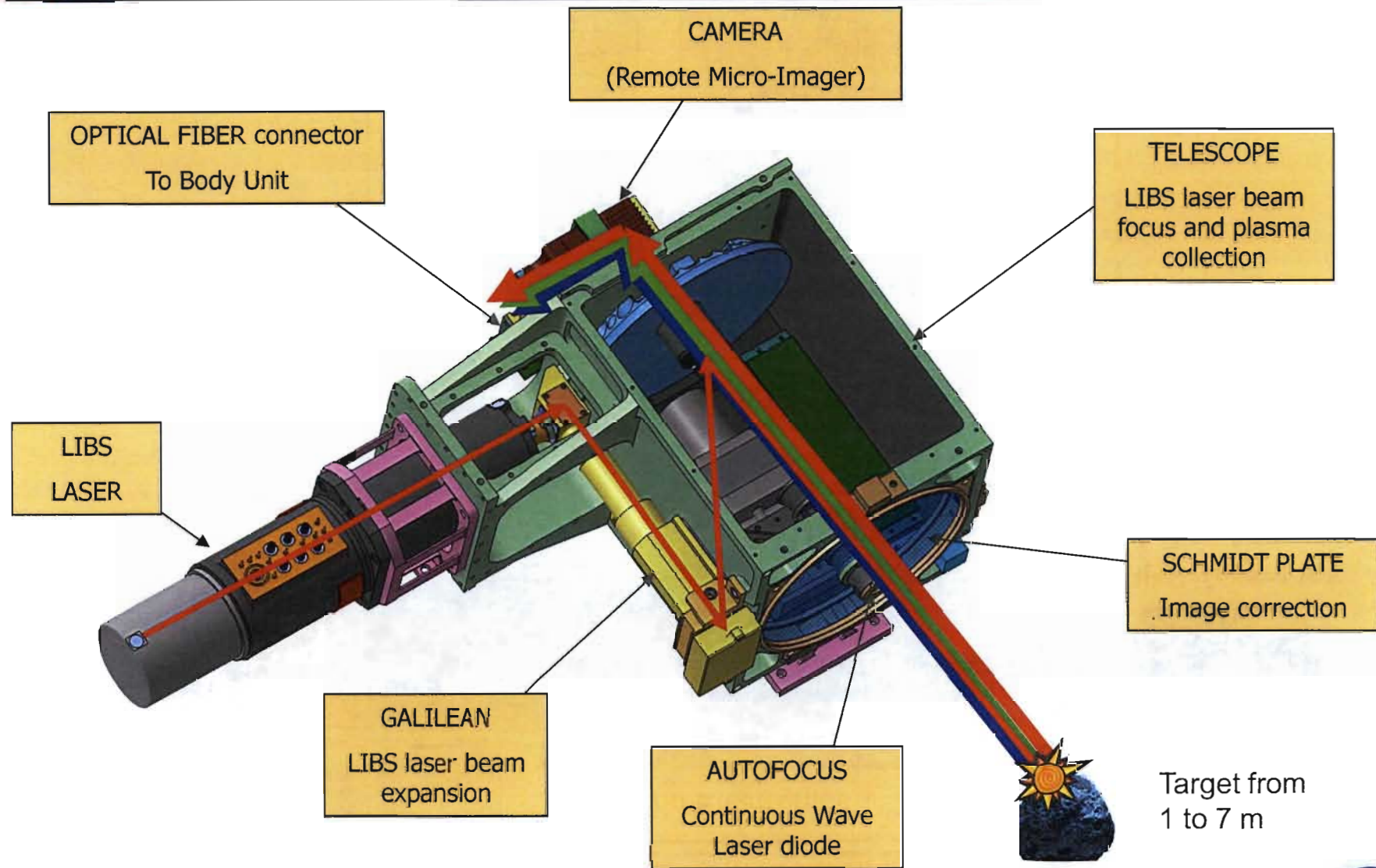
Derived Requirements

- Spectral range 242-800 nm
 - To cover C (strongest line 248 nm) and O (strongest line 777 nm)
- Spectral resolution
 - < 0.20 nm FWHM for < 470 nm
 - Separates 248 nm C line from Fe interference and 407.7 nm Sr line from Fe interference
 - < 0.65 nm FWHM for > 470 nm
 - Fewer and more widely spaced interferences in this spectral range
- Laser power density > 10 MW/mm²
 - Needed to create LIBS sparks
- Imager resolution ≤ 100 μ rad
 - To image LIBS analysis pits
- Laser rated to 5 million shots, passively cooled
- Requirements on transmission and signal-to-noise

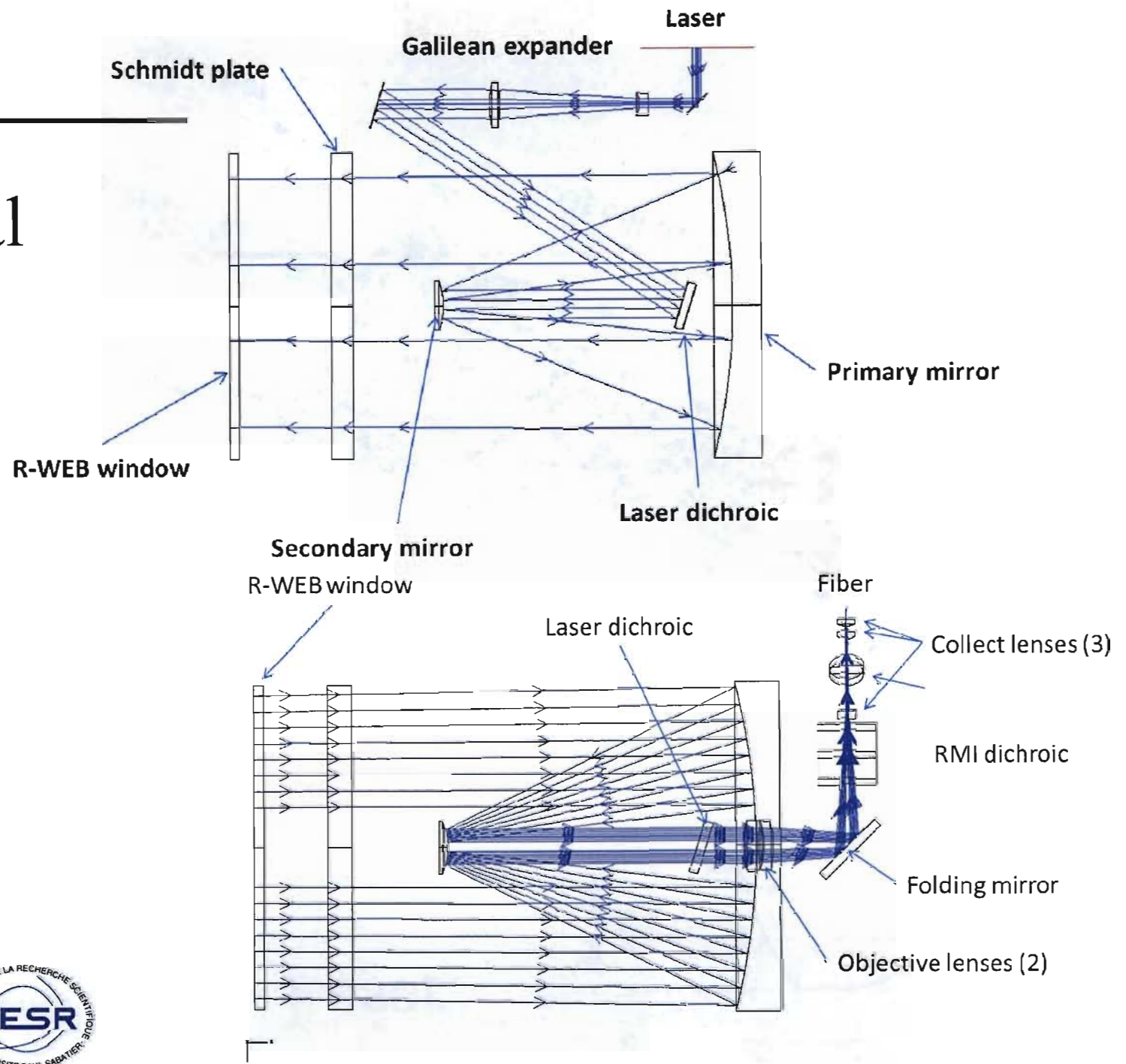
ChemCam Instrument Schematic



ChemCam Mast Unit : Optical Box

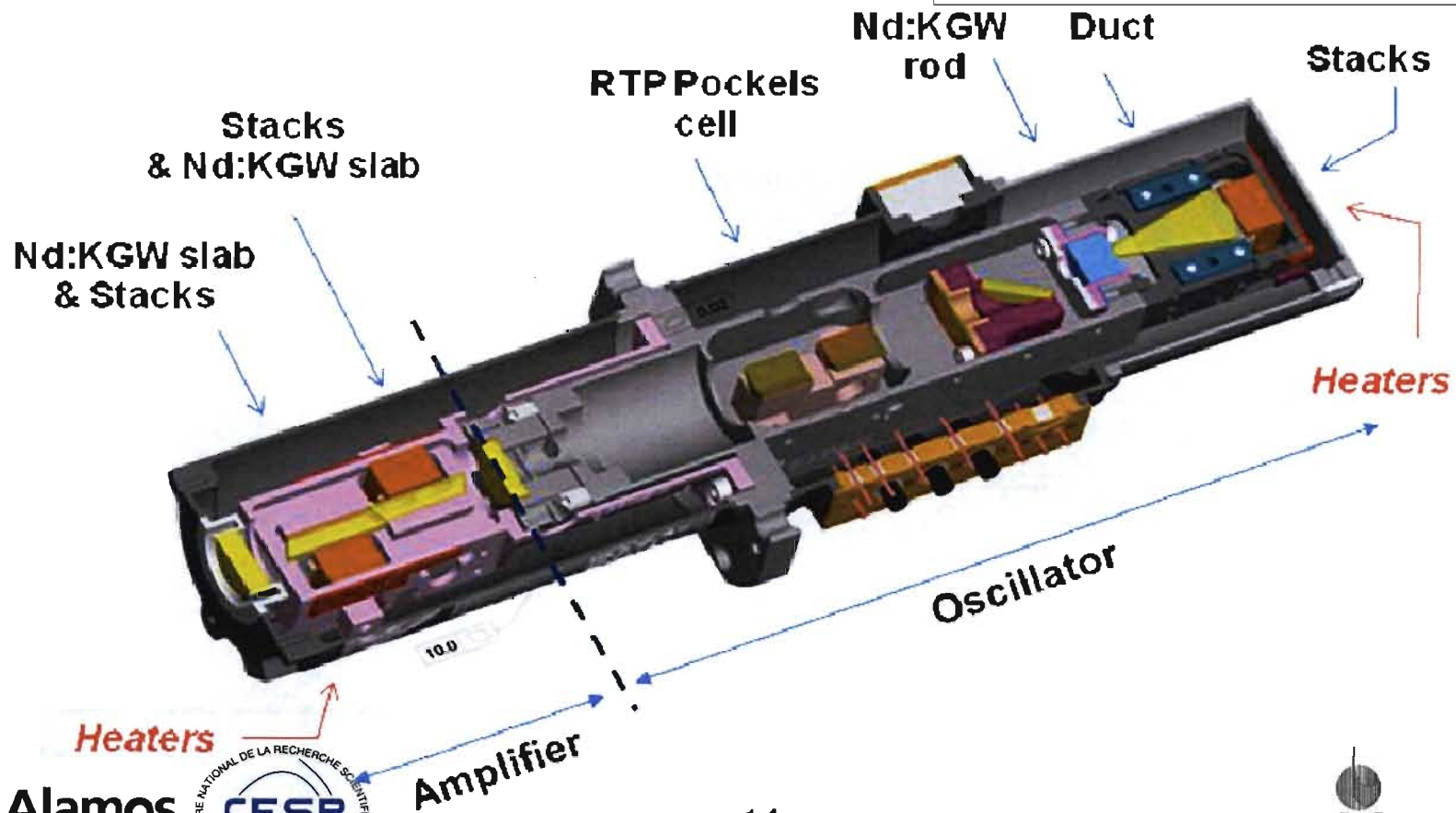
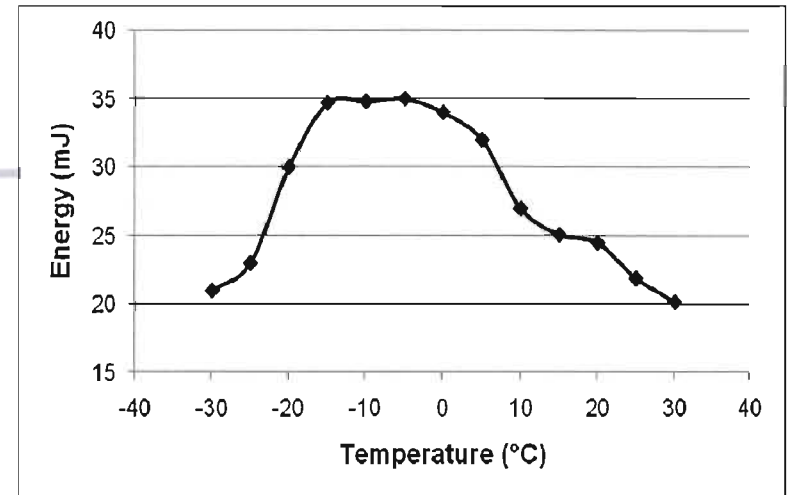


Optical Paths

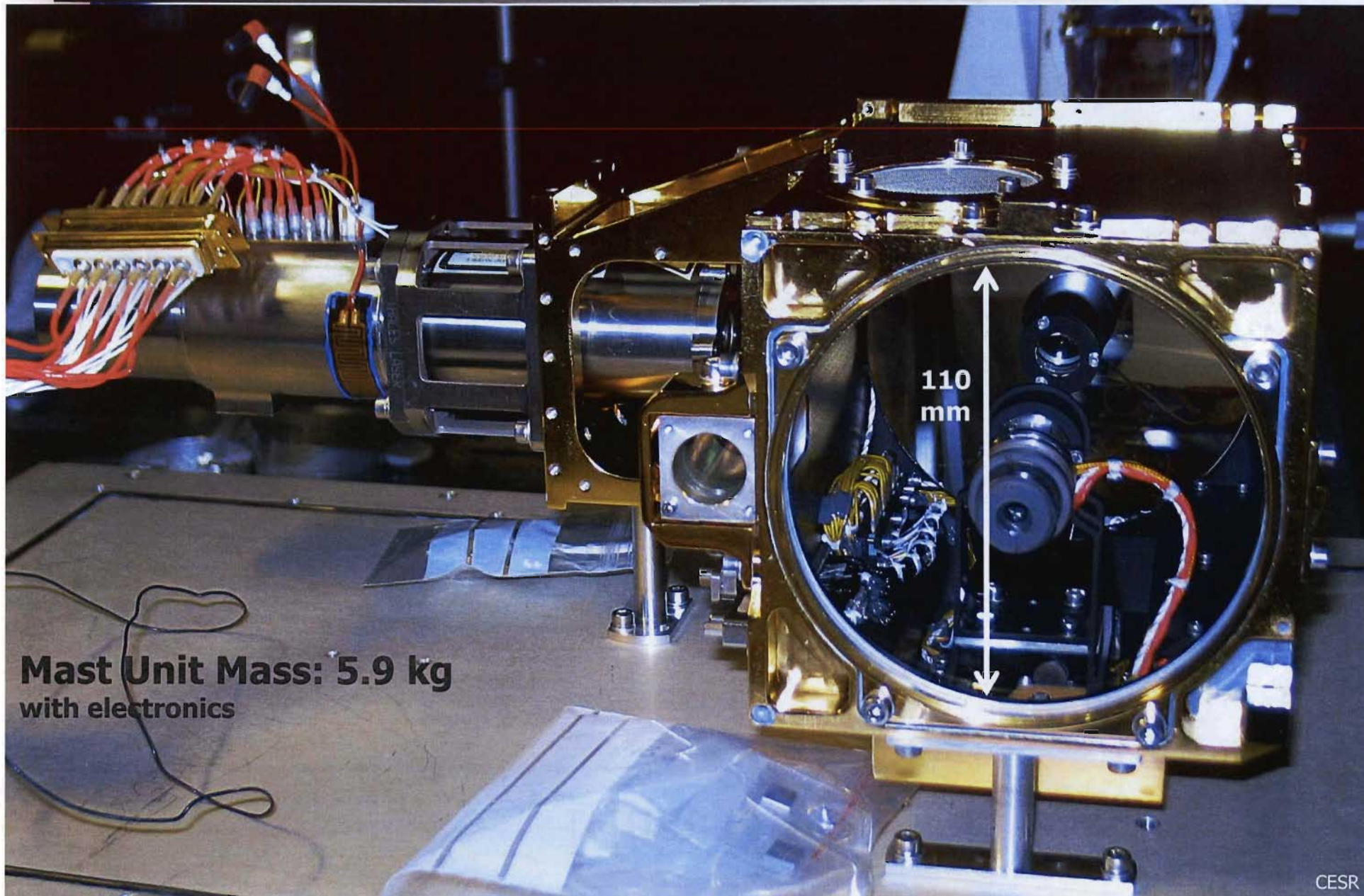


Laser

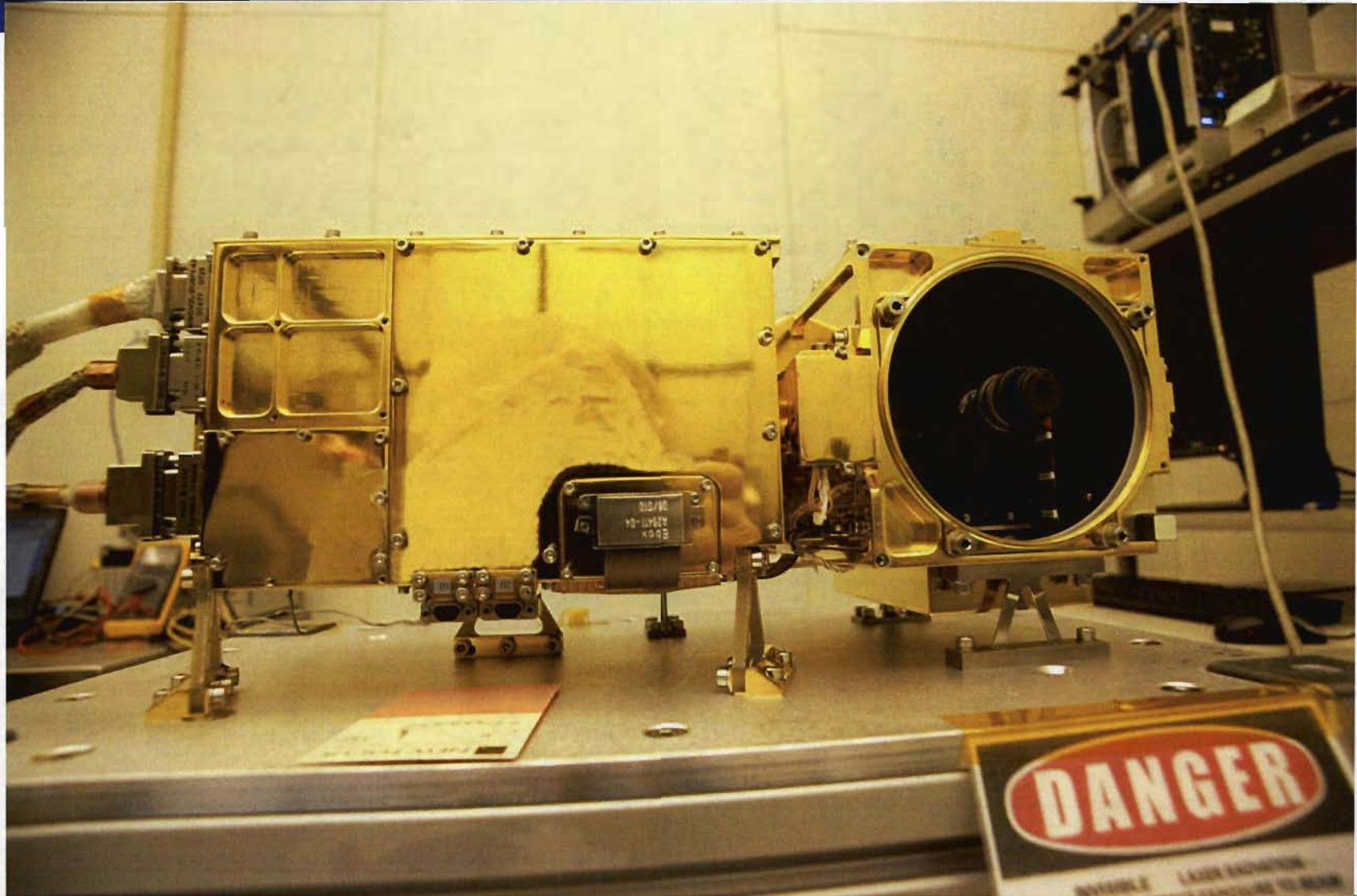
- Passively cooled
- Up to 35 mJ output
- ~500 g



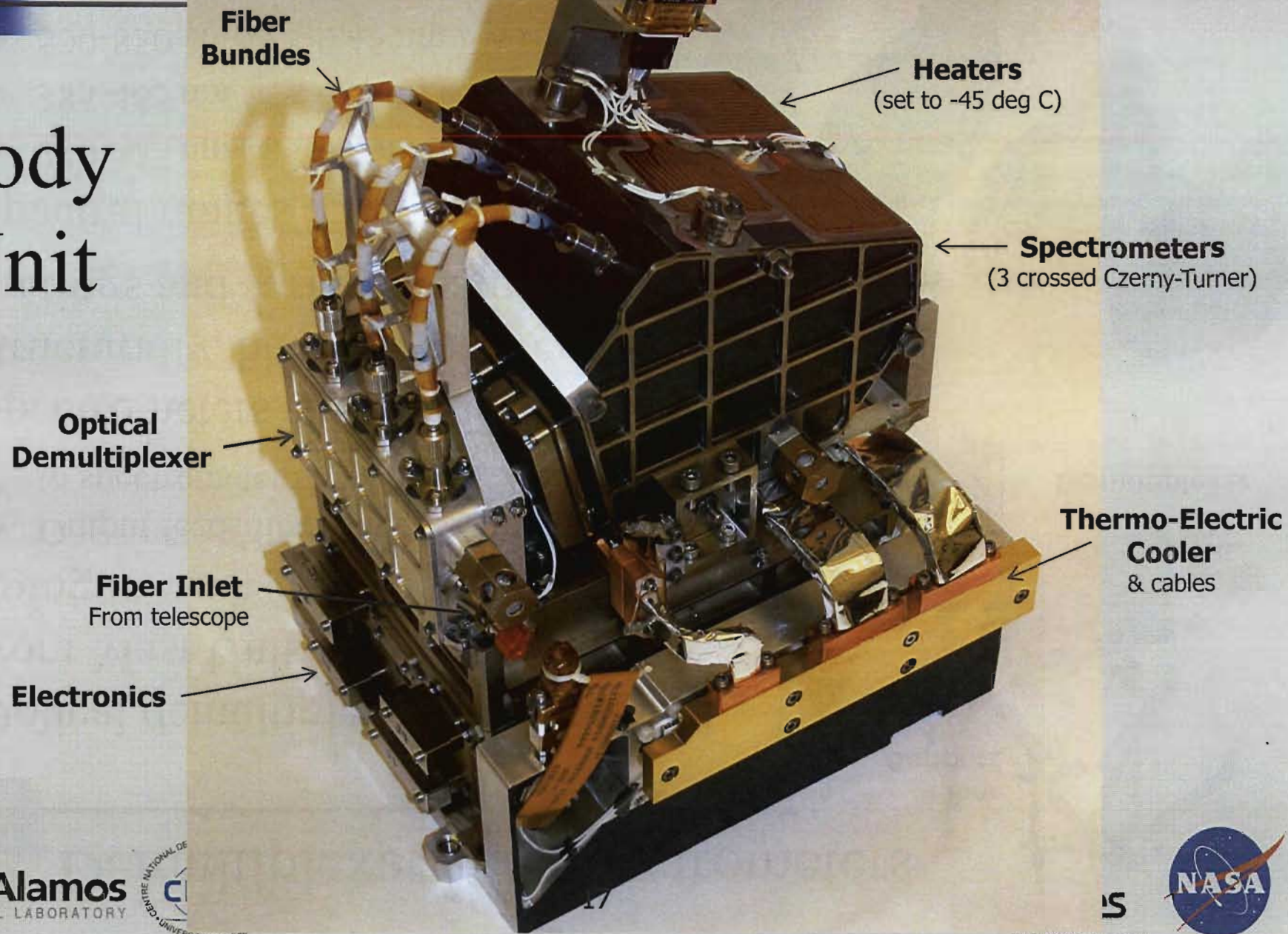
Laser & Telescope in Assembly



Mast Unit

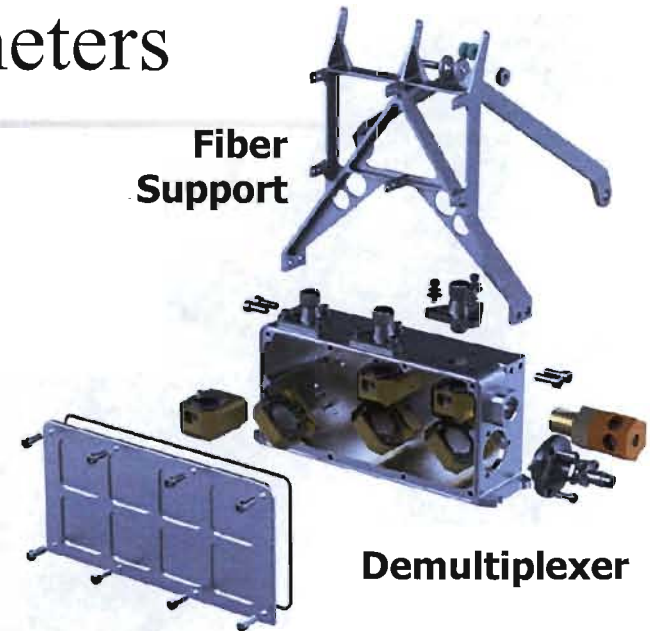


Body Unit



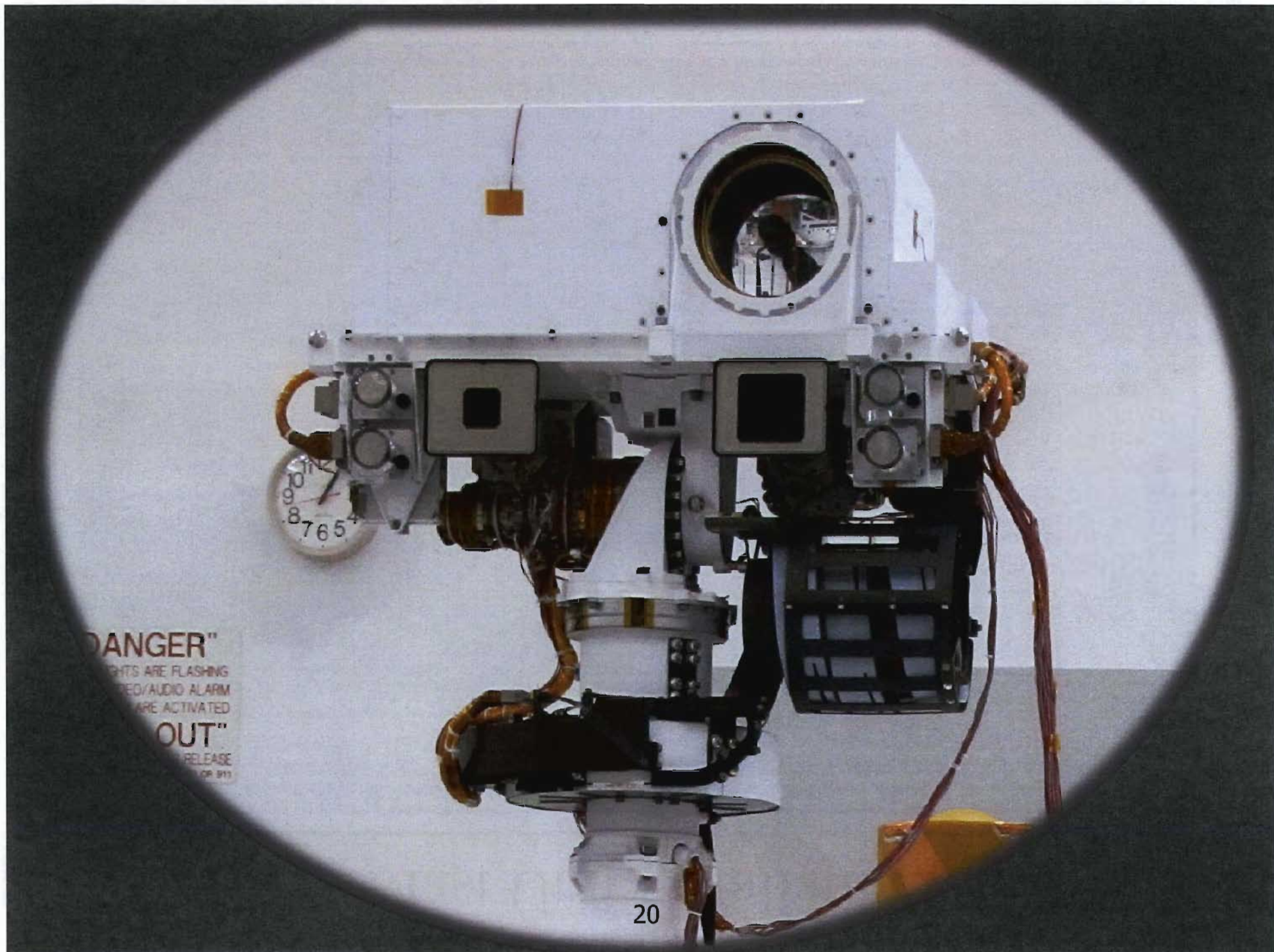
Demultiplexer and Spectrometers

- Optical demultiplexer receives light from Mast Unit, optimizes light going to each spectrometer
 - Output feeds fiber bundles linearly aligned to spectrometer slits
- Spectrometers are identical structurally, but with different gratings and surface coatings
- Spectral ranges
 - 240-335 nm @ < 0.2 nm FWHM
 - 385-465 nm @ < 0.2 nm FWHM
 - 500-850 nm @ < 0.45 nm FWHM



Mast Unit Installation





"DANGER"

FLASHERS ARE FLASHING

RED/AUDIO ALARM

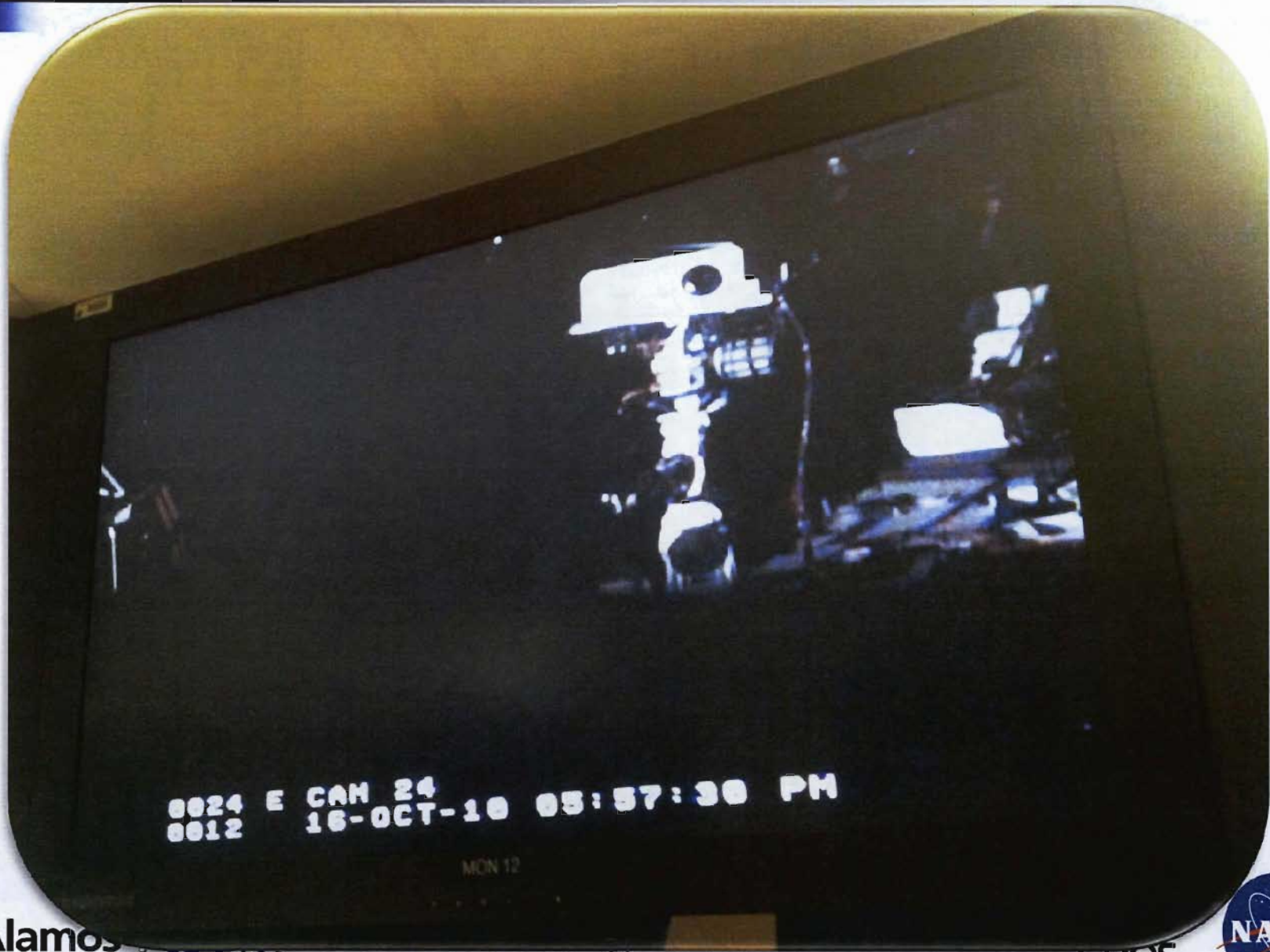
ARE ACTIVATED

"OUT"

RELEASE

OR 911

Rover During ChemCam Testing

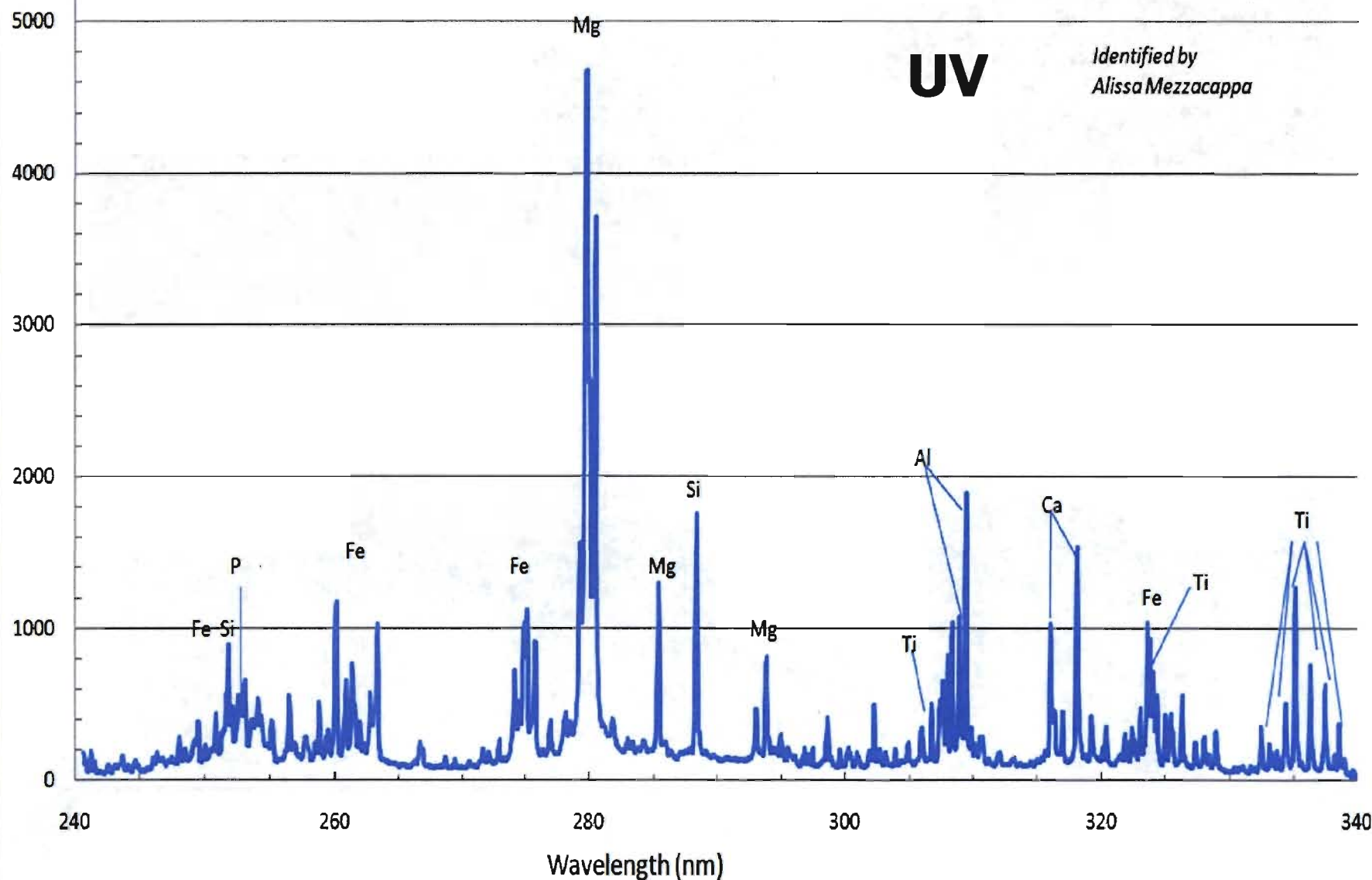


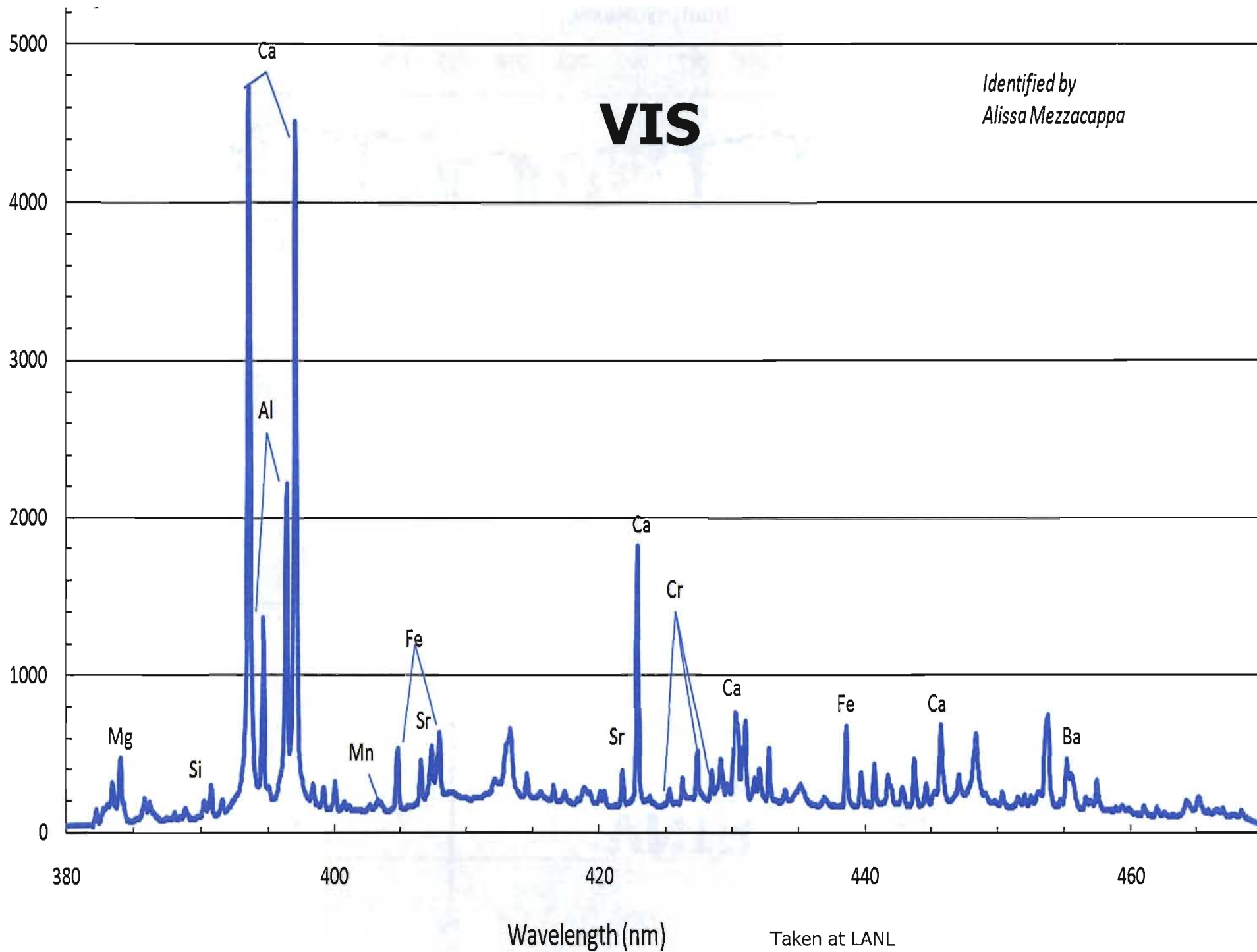
LIBS Spectrum

BT-2 basalt pressed powdr
3 m, 95 A during T-V
In 7 Torr CO2
No instrum. resp. correction

UV

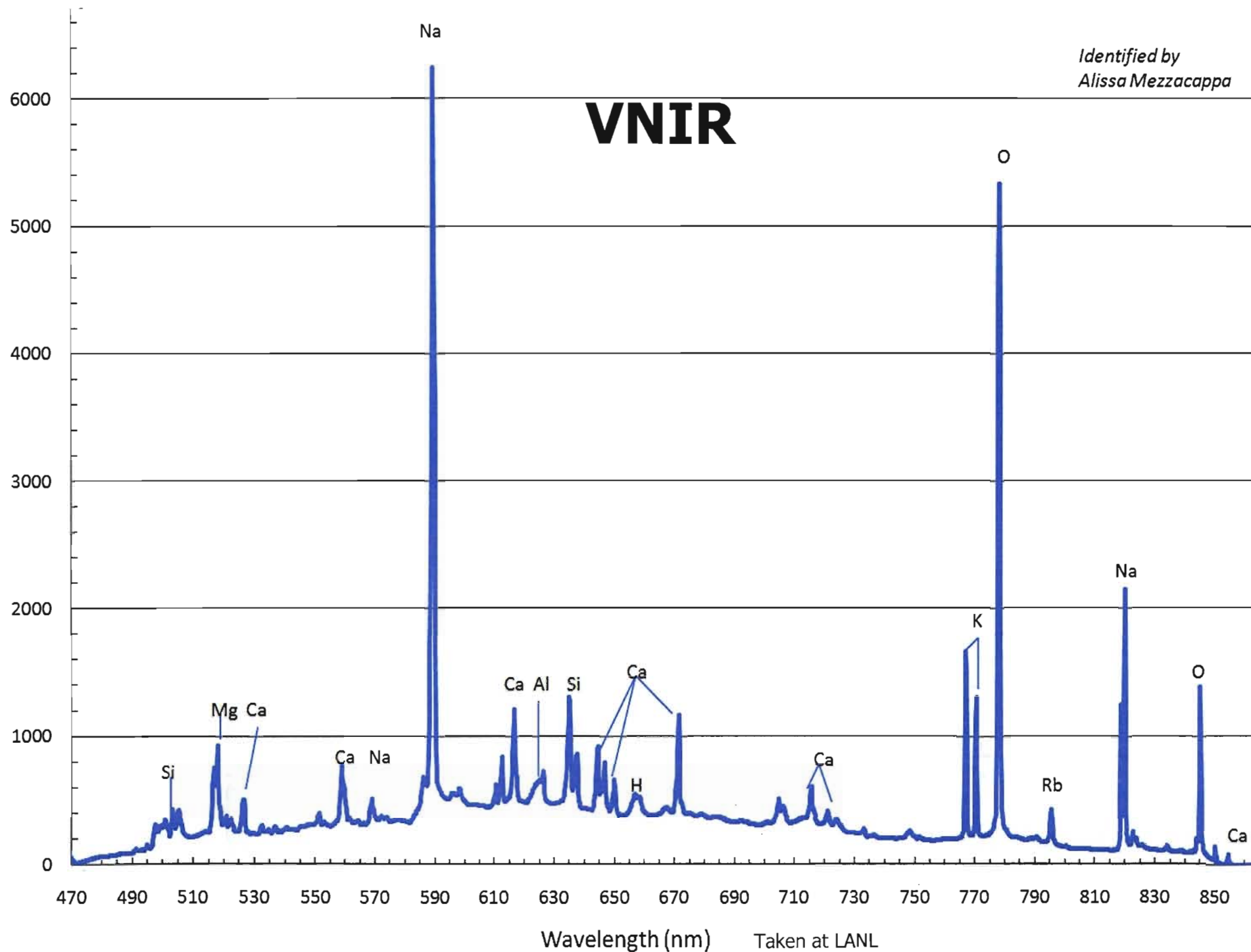
*Identified by
Alissa Mezzacappa*





VNIR

Identified by
Alissa Mezzacappa

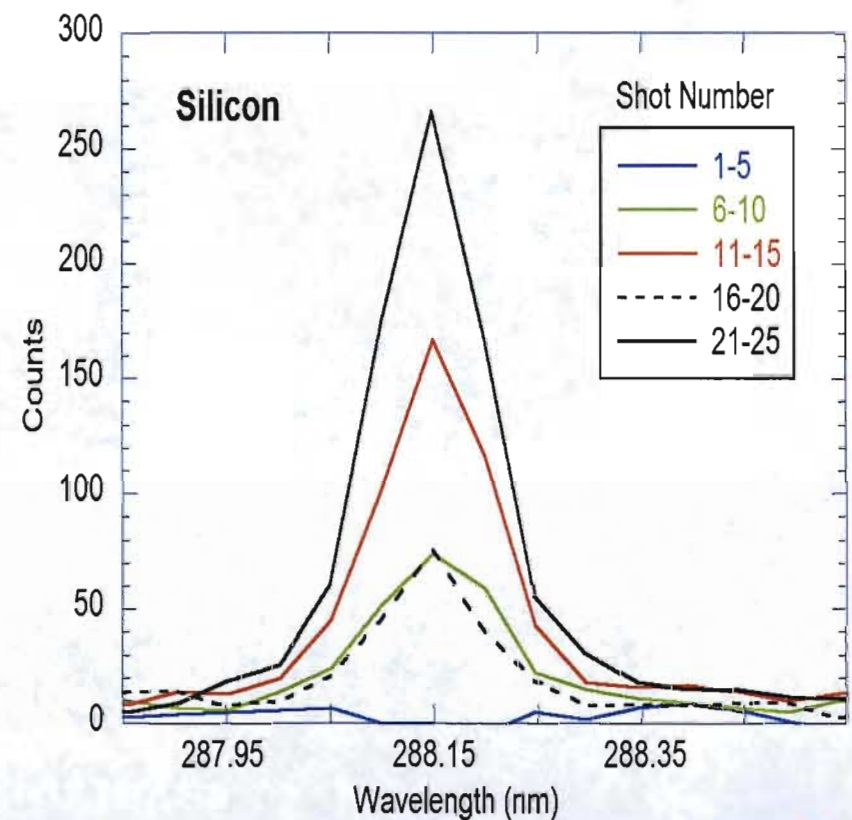


Dust Removal

- Tested at 3.5 m in Mars atmosphere
 - Several mm of dolomite dust on basalt disk
 - Watch silicon peak grow in



← 30 mm →





Mars Pressure @ 2.86 m 25 μm layer of dust

50 shots, 10 mJ

Next Slide

5 shots, 7.5 mJ

10 shots, 10 mJ

Diameters between
1.5 and 2.4 mm

← 26 42 mm →

265-325 nm

5

Basalt

4

3

(Transition)

Fe

Mg

C (Weak)

Mg

Si

Mg

Al

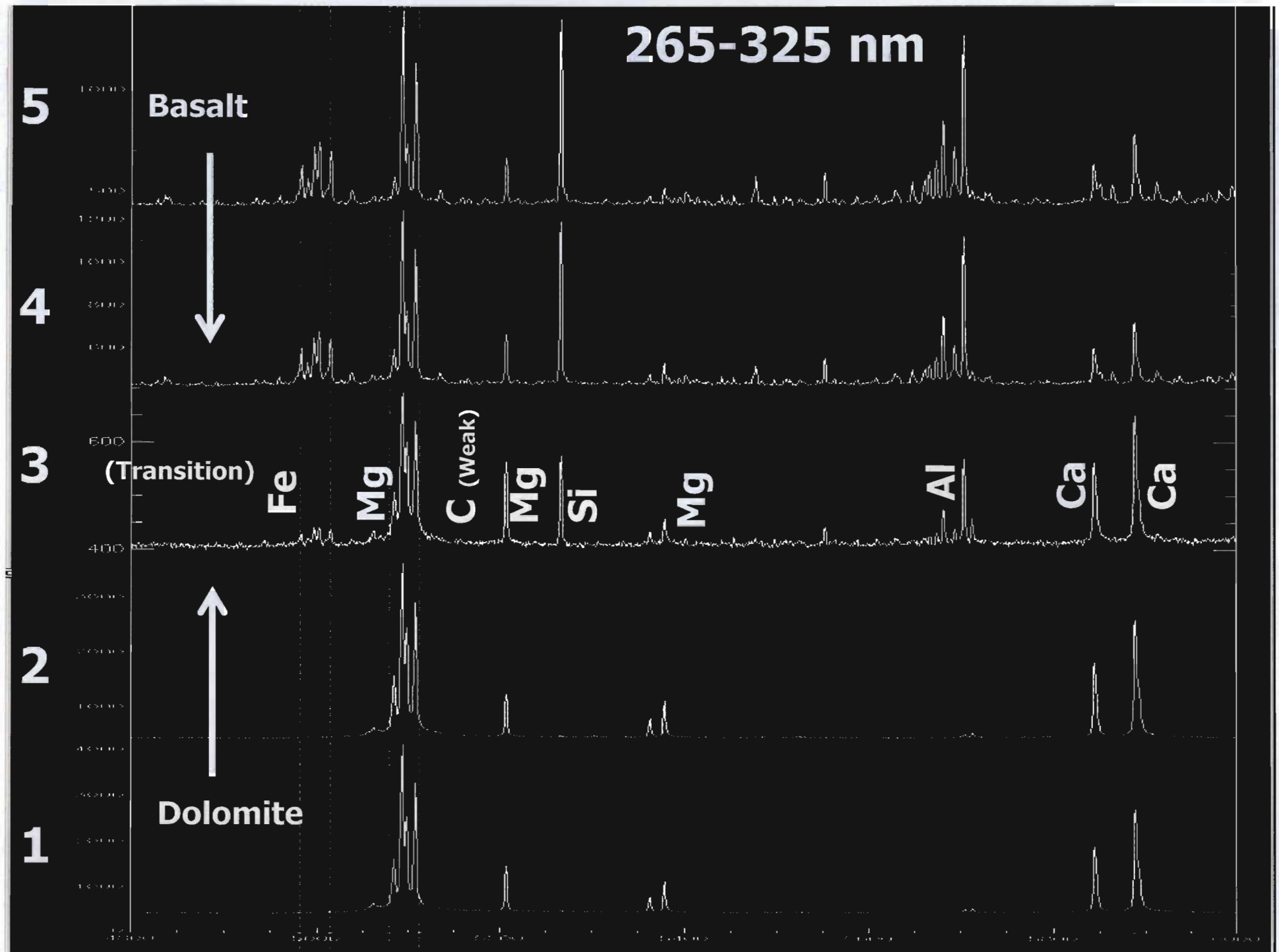
Ca

Ca

2

1

Dolomite

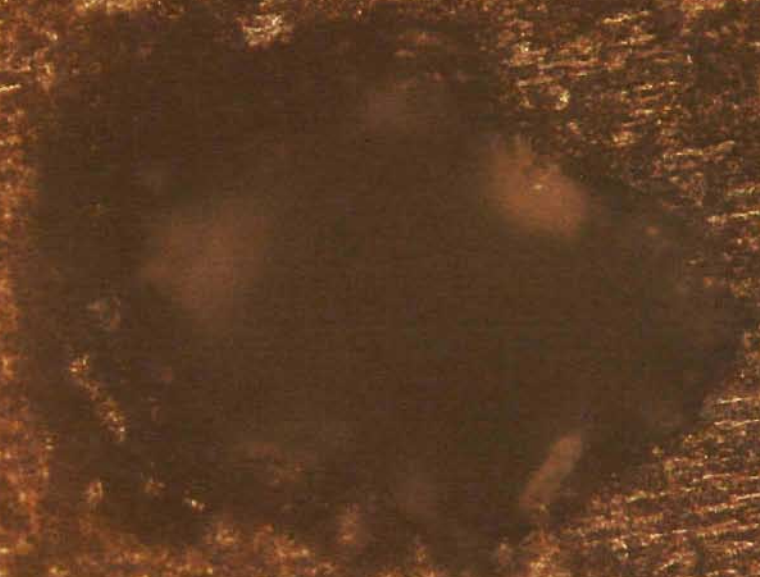




Depth Profile in Carbonate @ 3 m



500 shots in carbonate @ 3 m



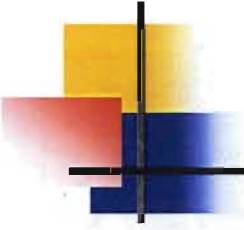
500 shots in carbonate @ 3 m

500 shots in carbonate @ 3 m

500 shots in carbonate @ 3 m

500 shots in carbonate @ 3 m

400 um depth



LIBS Data Processing

- Sanity check and de-noise
- Subtract non-laser background file
- Remove electron continuum
- Wavelength calibration & pixel re-sampling
- Correct for instrument response
- Normalize and correct for distance



LIBS Data Analysis—Test for Quality

- Use pressed rock powders for homogeneous samples
- Averaged ~50 spectra on the same spot
- Analyzed 4 different spots per sample
- 11 different samples analyzed
- Classification methods:
 - Euclidean Distance
 - Sammon's Map
 - Independent Component Analysis
- Quantification: Partial Least Squares Regression (PLSR)

Projection and clustering methods

Igneous rocks at 5 m thermo-vacuum tests

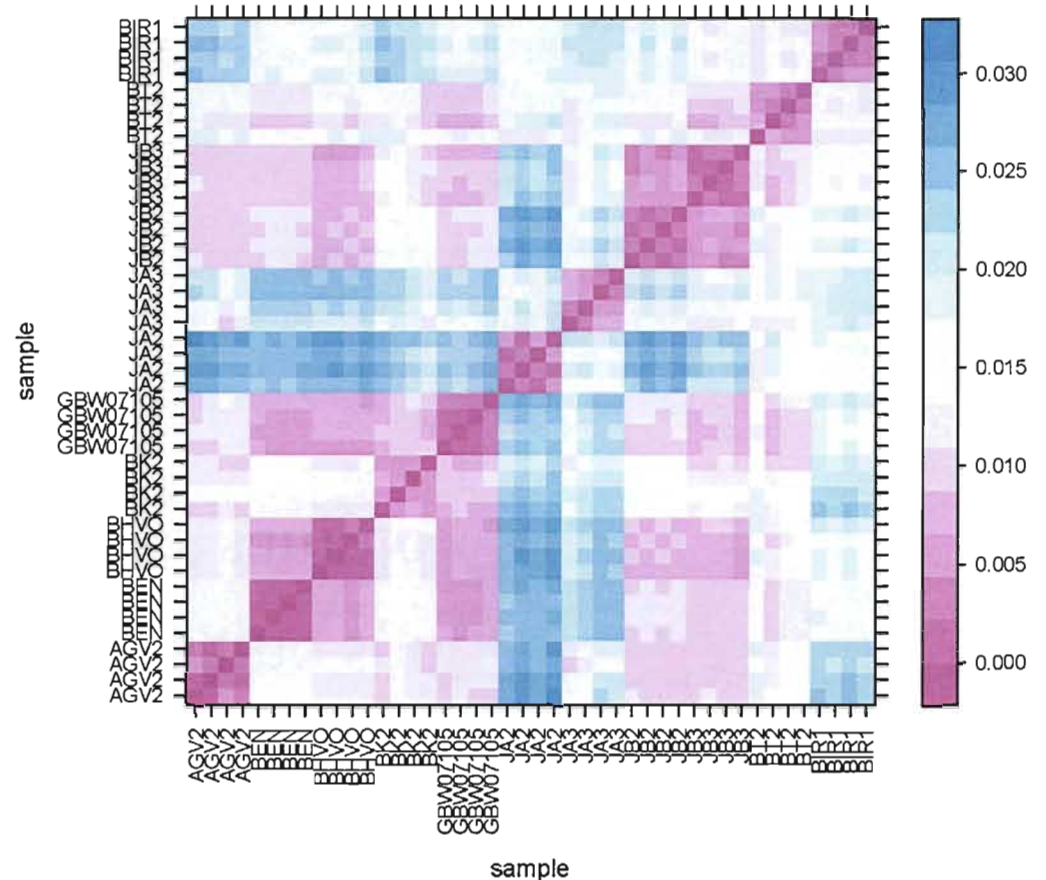
Euclidean distance matrix of the 44 spectra used

Euclidean distance gives a good clustering of the different samples

4 clusters can be seen: BIR1; JA2; JA3; other samples

Useful to detect outliers in the dataset

distance matrix of the 44 spectra used



3. Projection and clustering methods

Igneous rocks at 5 m thermo-vacuum tests

Non-linear Bi-dimensional
projection minimizing:

$$E = \frac{1}{\sum_{i < j} d_{ij}^*} \sum_{i < j} \frac{(d_{ij}^* - d_{ij})^2}{d_{ij}^*}$$

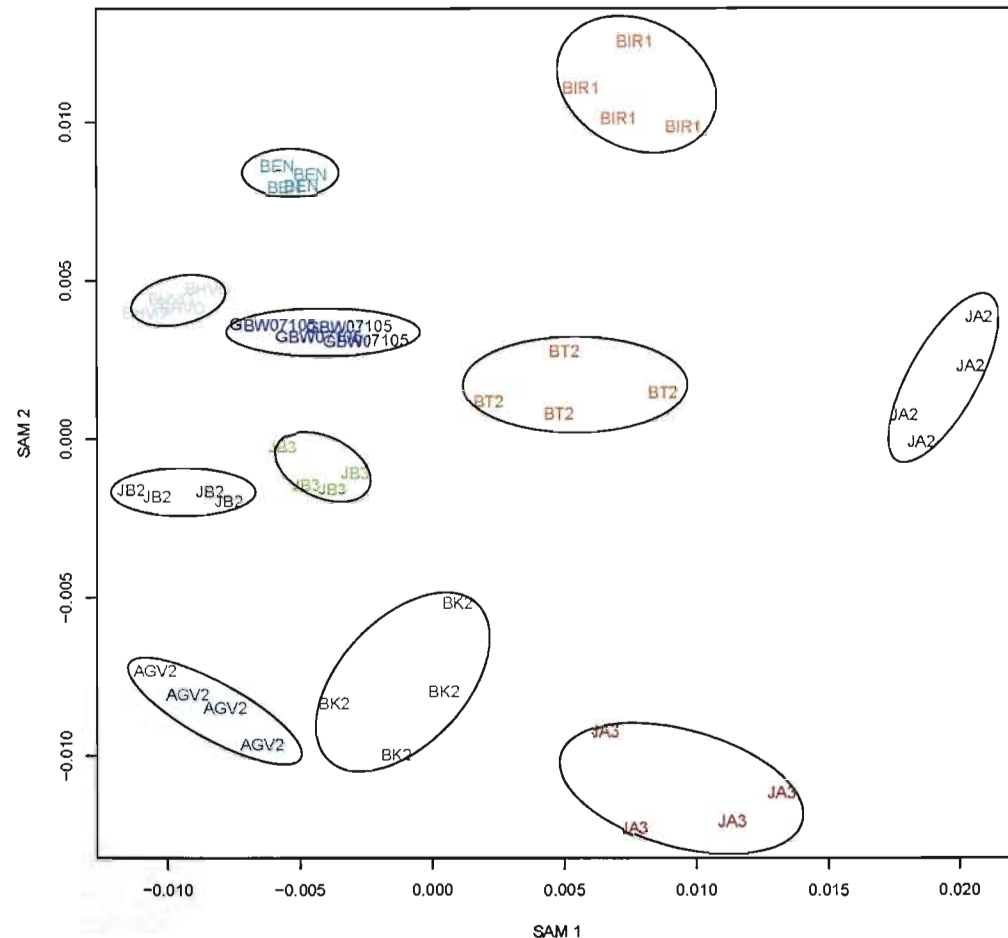
d_{ij} = initial space distance between i and j

d_{ij}^* = map distance between i and j

• In this case 2 times better than PCA for visual representation of the dataset.

ICA planned to be used by ChemCam

Sammon's map



Quantification of elemental composition

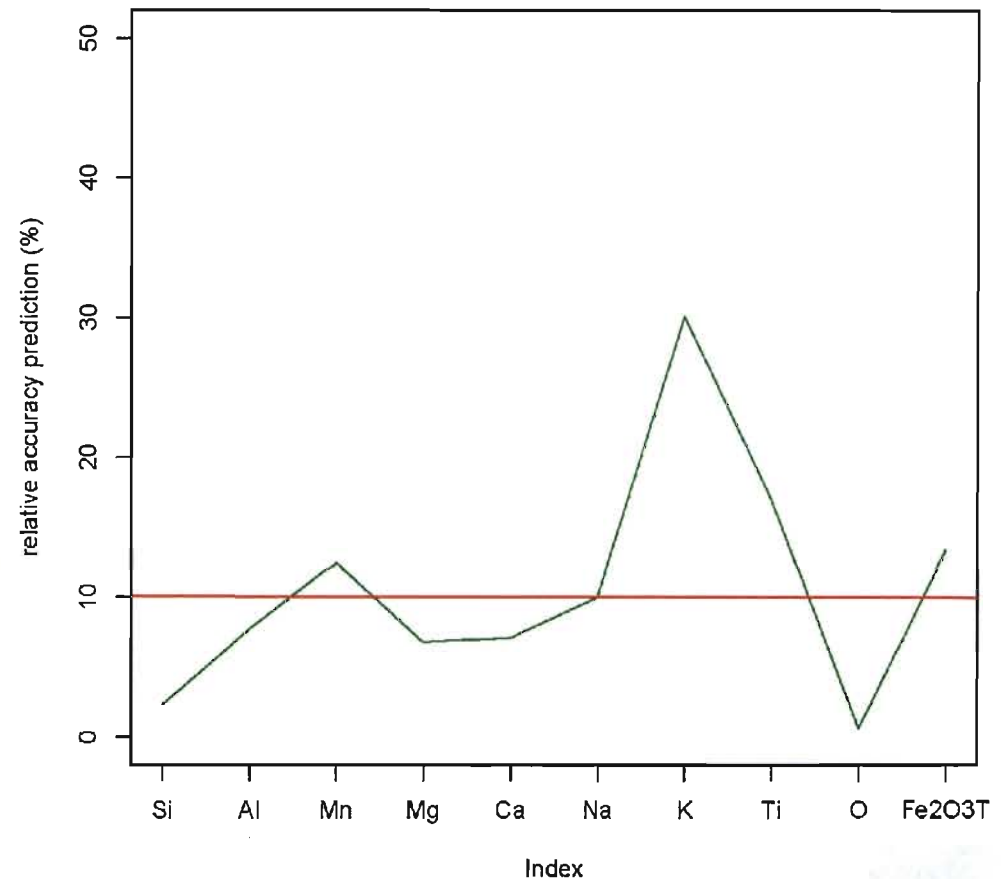
Results PLSR at 5 m thermo-vacuum tests for 11 igneous standards

Using PLSR, the median of the relative accuracy predictions for **unknown samples** is shown (one sample left out statistics).

The accuracy of the predictions are typically of the order of **10% or lower**.

The quantities of Mn, K, Ti to be predicted are the lowest ($<10^{-3}$) which can explain the relative accuracy increase.

5 m PLS relative accuracy prediction unknown sample



Quantification of elemental composition

Results PLSR at 5 m thermo-vacuum tests

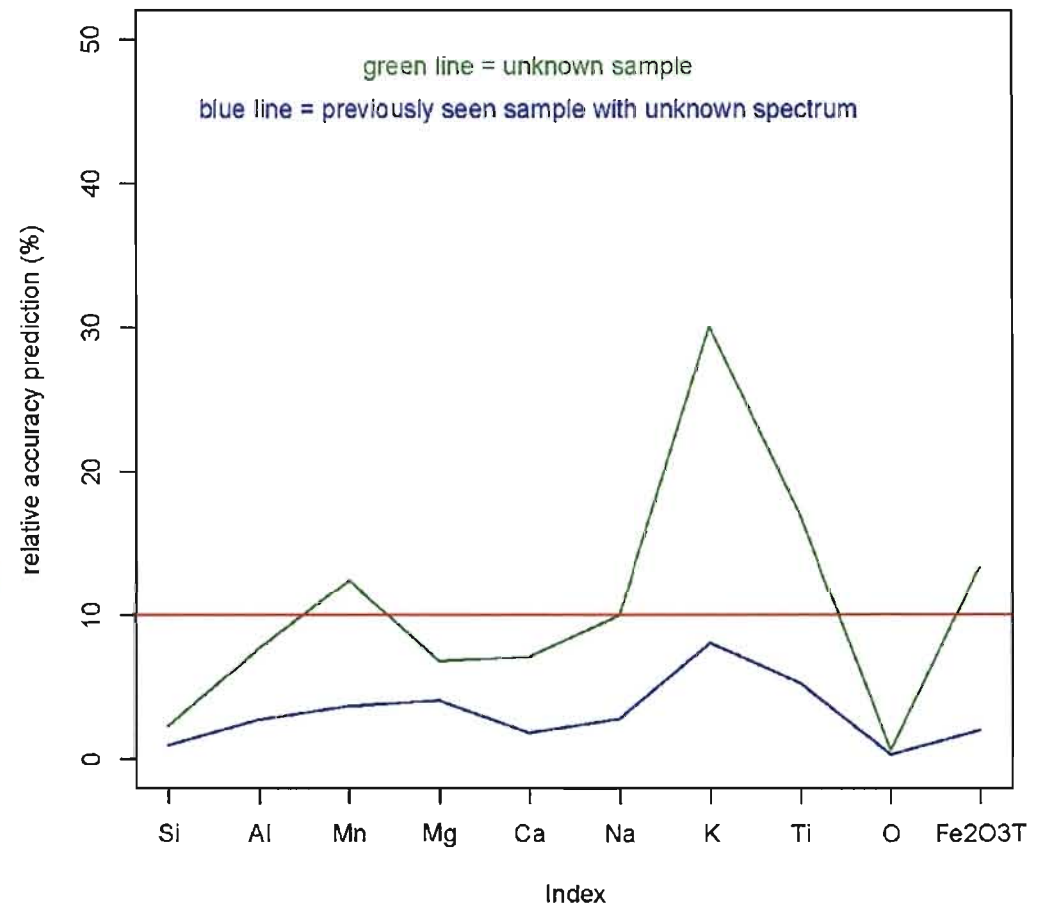
Here, the PLS model includes some spectra of the sample we are trying to predict.

The accuracy of the predictions are **10% or lower for all elements.**

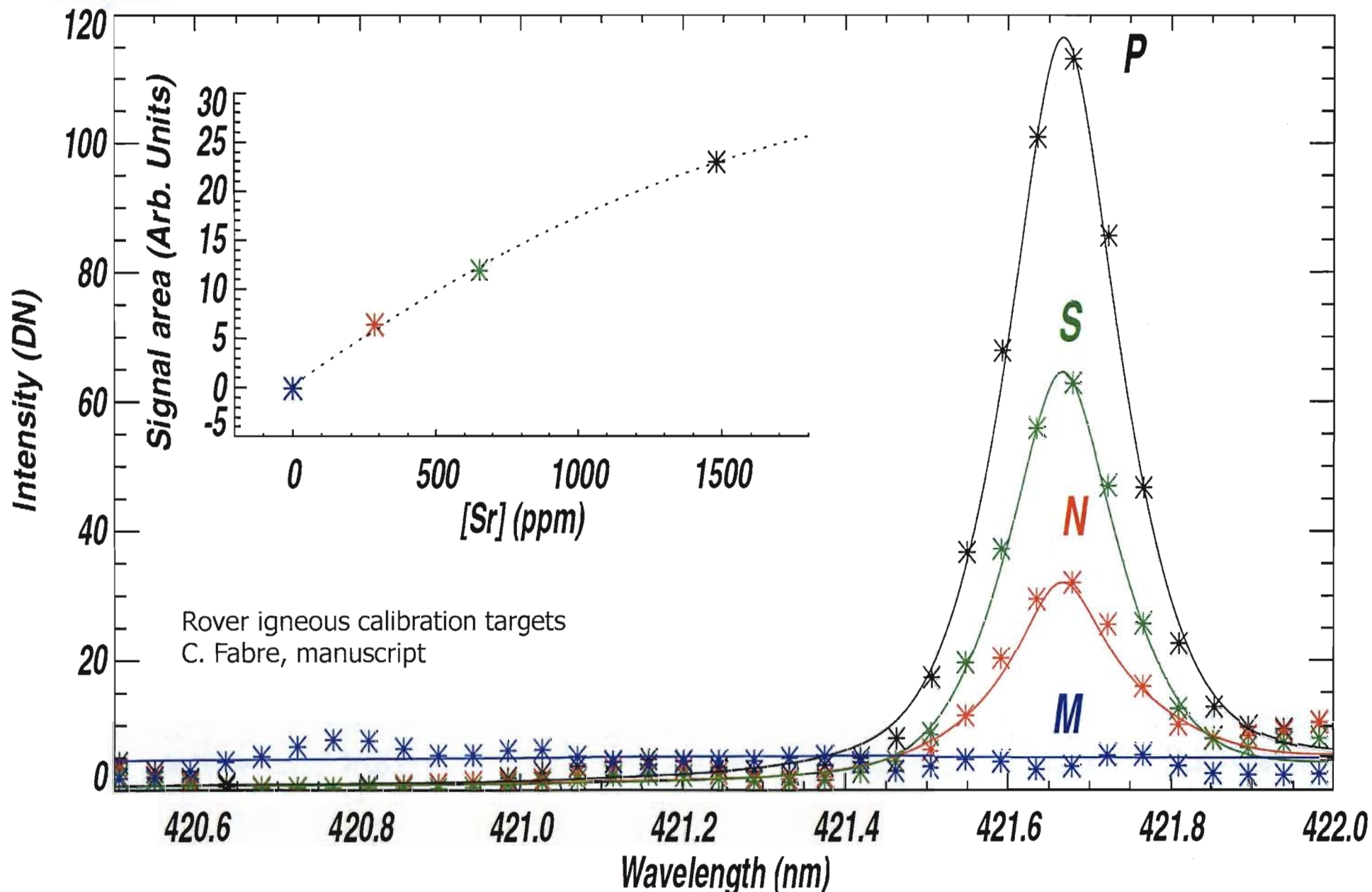
The predicted spectrum is never used to generate the model.

Calibration based on most similar analogues will give best results.

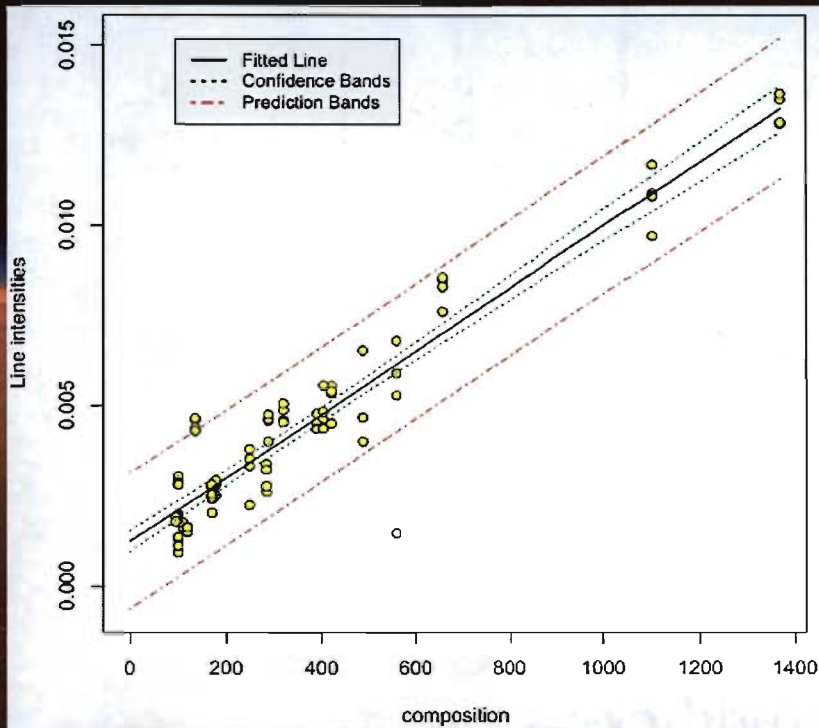
5 m PLS relative accuracy prediction



LIBS Minor & Trace Elements--Sr



LIMITS OF DETECTION



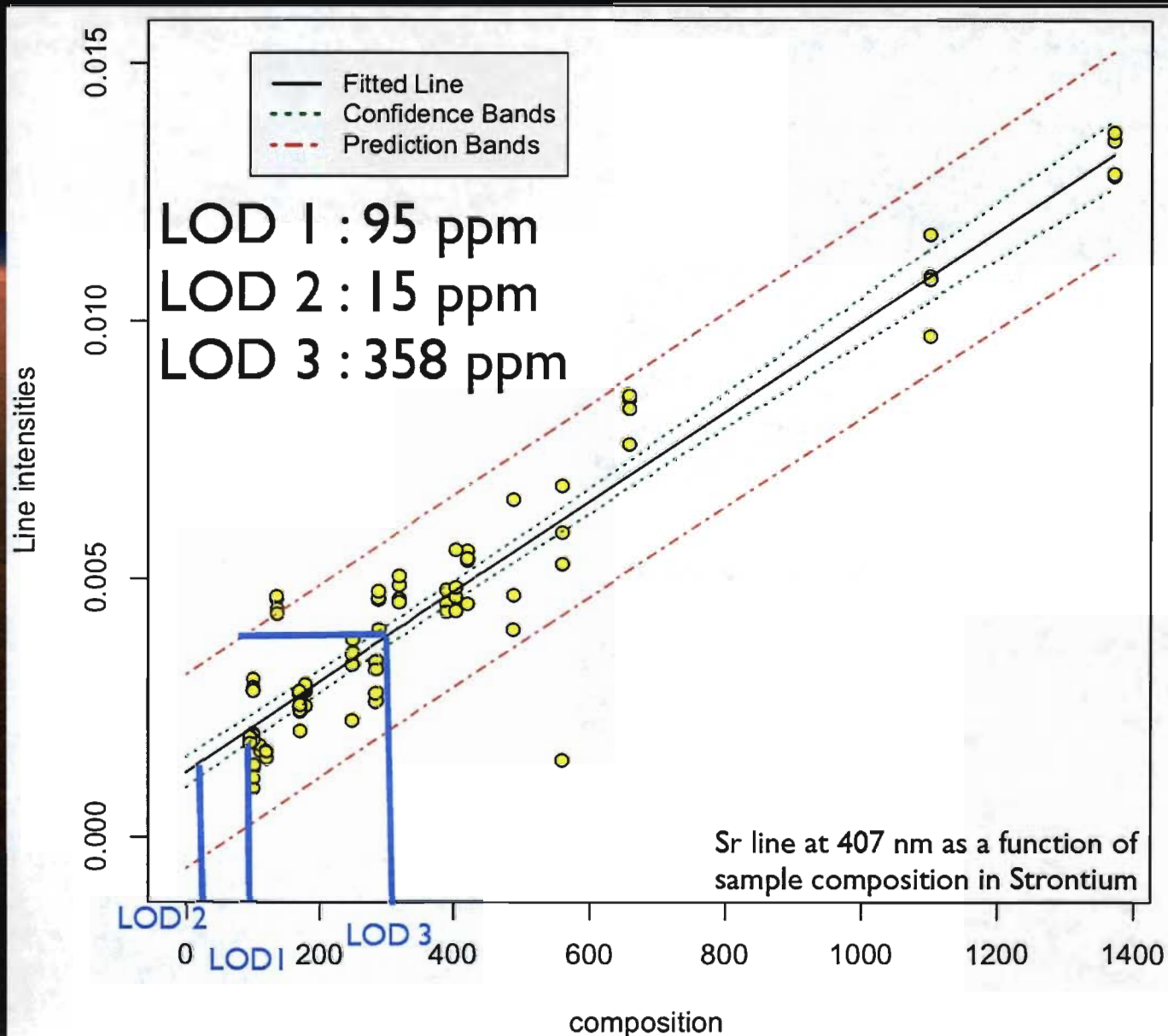
Sr line at 407 nm as a function of sample composition in Strontium

- LOD 1 : First sample with a line “above the noise”
- LOD 2 : Extrapolation of LOD 1 for the lowest concentration
- LOD 3 : Taking into account all the uncertainties

Usually : $\text{LOD 2} < \text{LOD 1} < \text{LOD 3}$



LIMITS OF DETECTION



LIMITS OF DETECTION

FIRST RESULTS

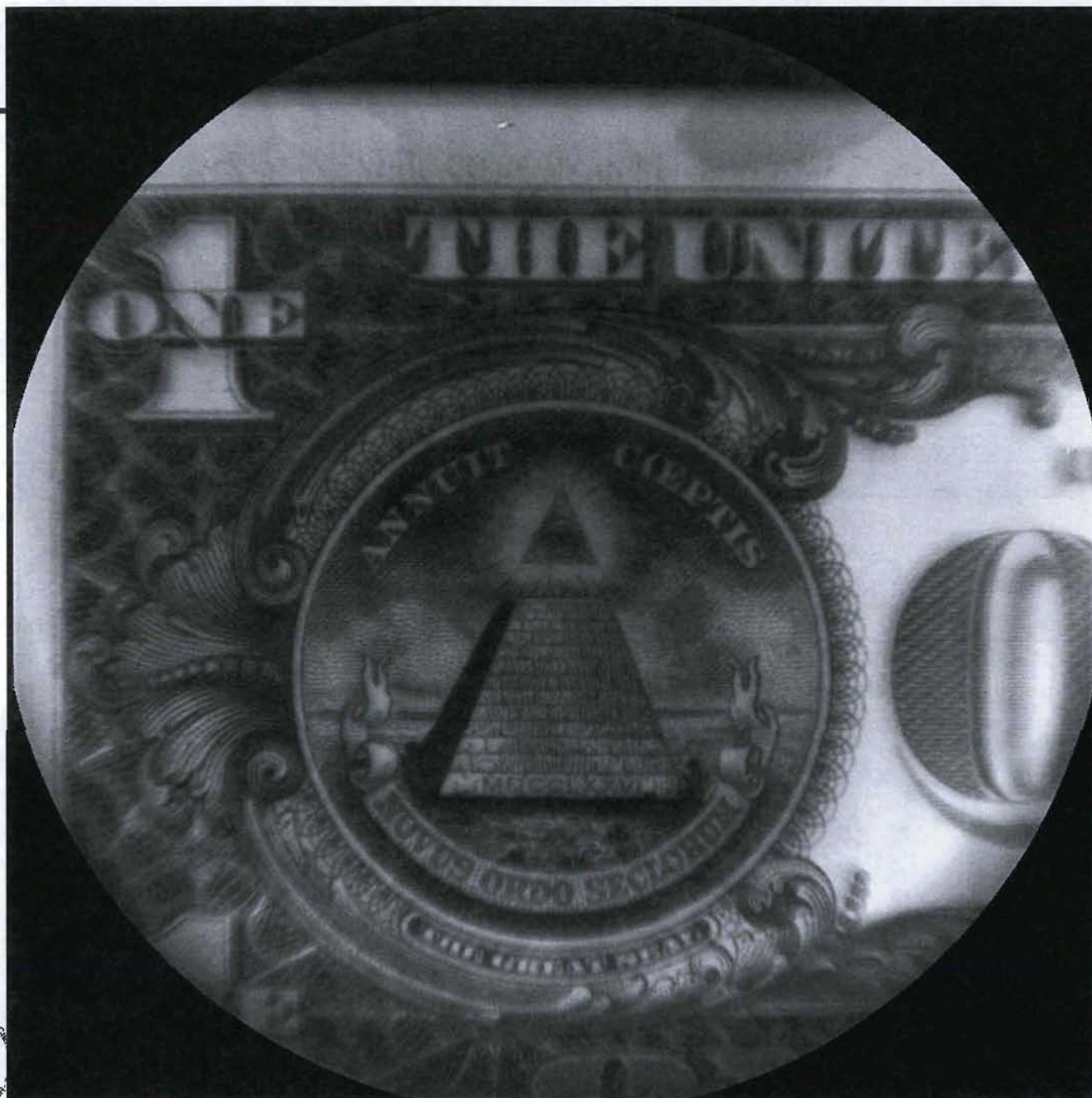
Element	λ (nm)	LOD1 (name of the sample)	LOD2	LOD3	Correlation	Limitation of high composition and comments
Cr I	425	360 (BE-N)	9.7	445	0.58	compositions < 500 ppm only
Ba II	455	208 (JB-2)	45	1245	0.70	without STDS-1 (outsider)
Ba I	455	208 (JB-2)	46	973	0.82	without STDS-1
H I	656	503 (Ultramafic)	320	4966	0.75	
K I	766	16 (JDO-1)	58	13843	0.94	
K I	766	16 (JDO-1)	13	12401	0.95	polynomial correction
K I	770	16 (JDO-1)	97	14913	0.93	No
K I	770	16 (JDO-1)	12	12195	0.95	polynomial correction
Li I	671	5 (BHVO-2)	0.3	25	0.98	compositions < 151 ppm only
Mn I	403	303 (NAu2-MID-S)	63	1330	0.90	No
Mn II	294	267 (Green-Rvr)	65	1465	0.88	No
Rb I	780	30 (STSD-1)	11	42	0.94	compositions < 170 ppm only
Sr II	407	95 (NAu2-MID-S)	15	358	0.95	compositions < 1800 ppm only





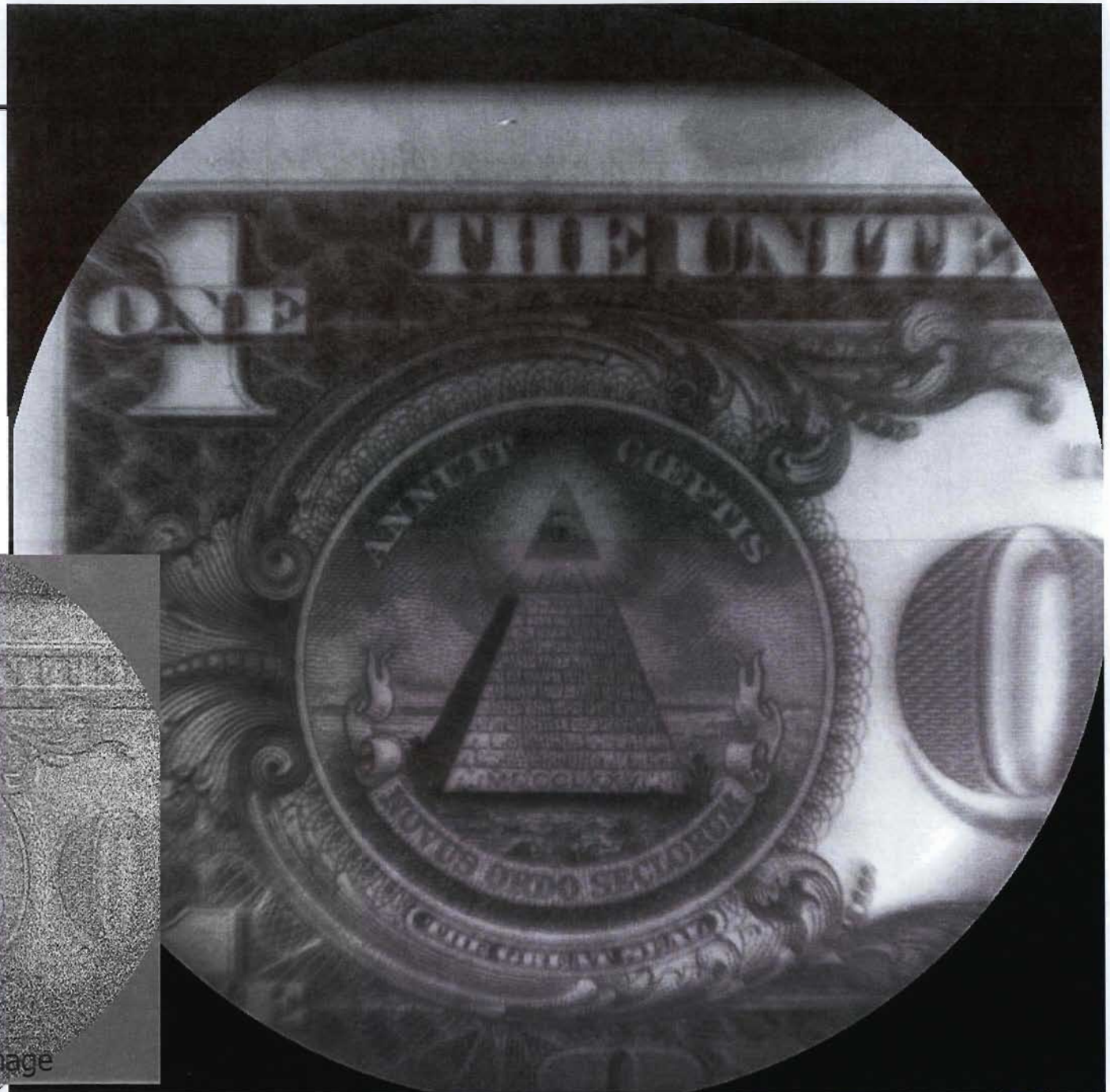
ChemCam Micro- Imager Performance

\$1 @ 3 m distance

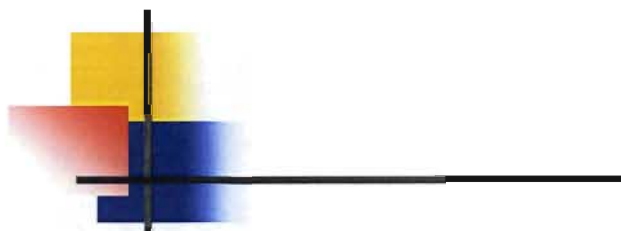




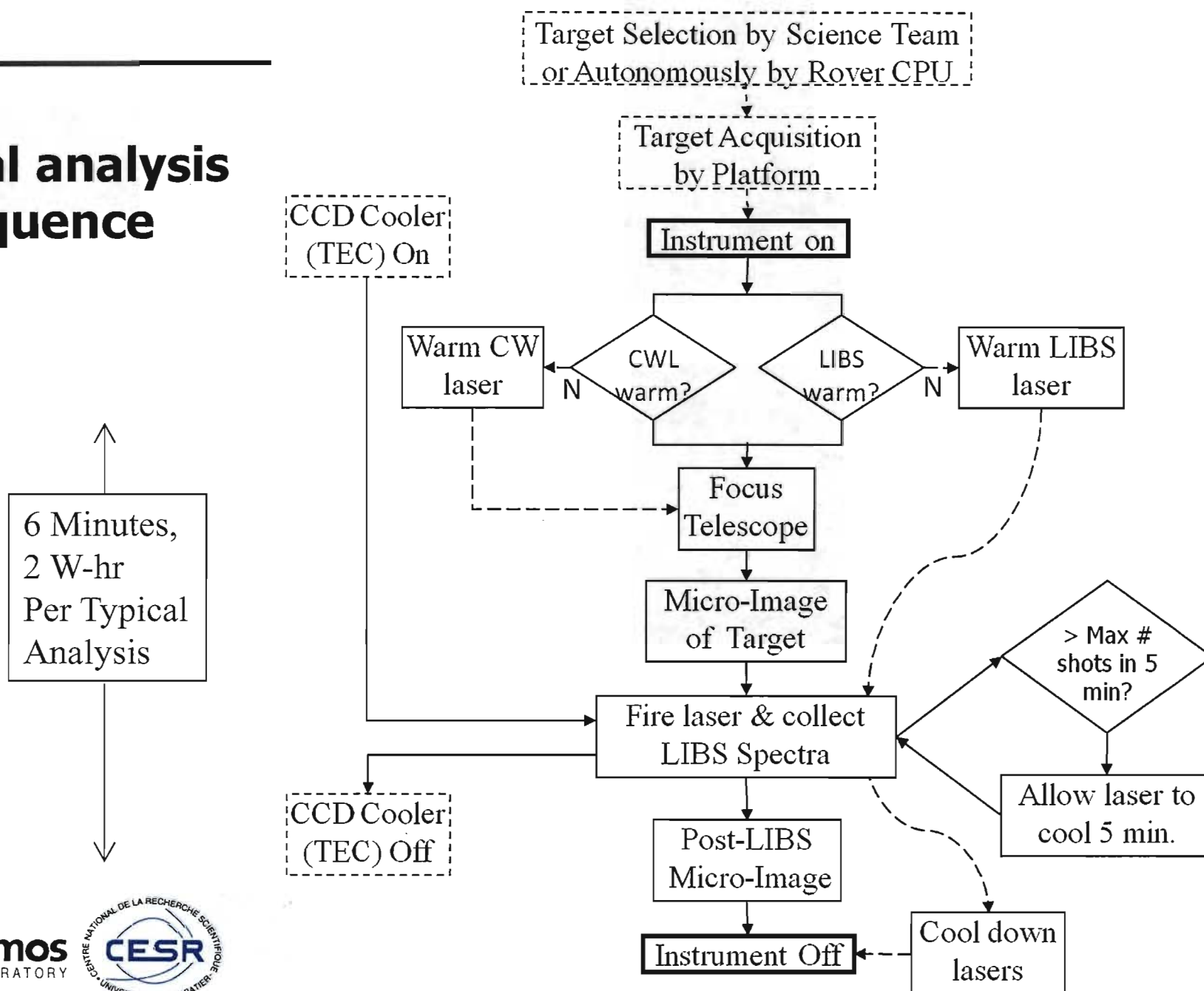
ChemCam Micro- Imager Performance



Stretched Difference Image

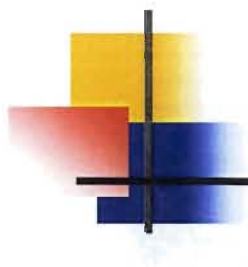


Typical analysis sequence





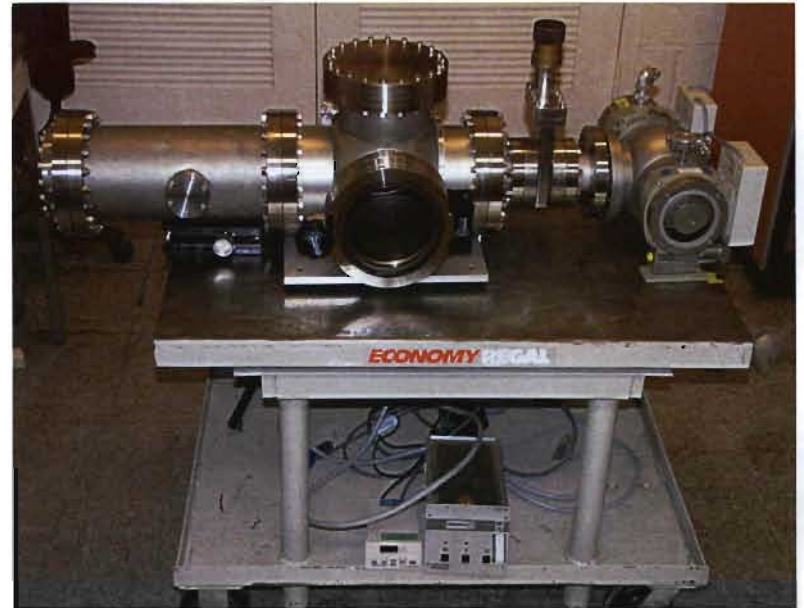
- [illegible]



LIBS ON OTHER PLANETS

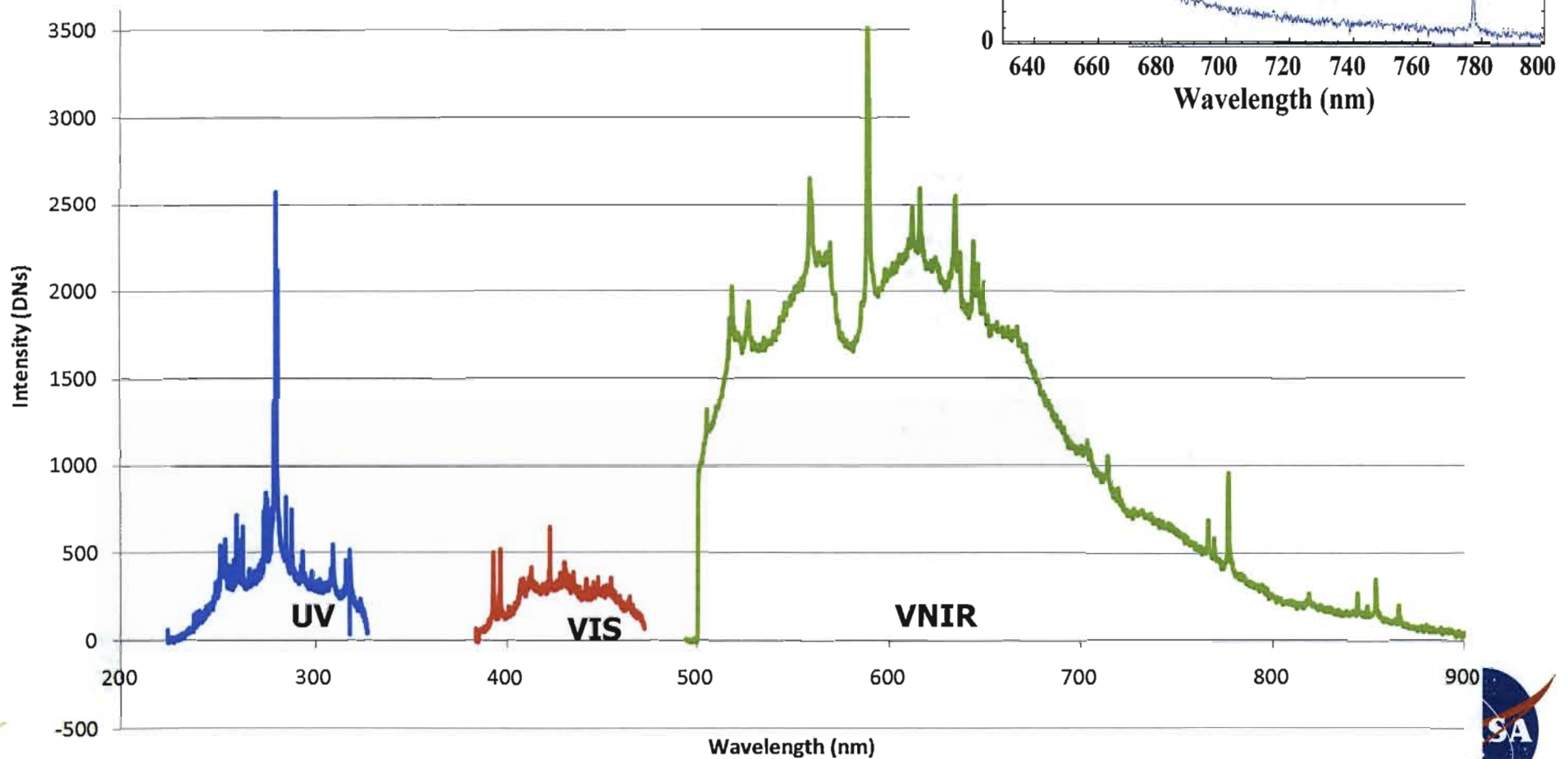
Lunar LIBS Experiment

- LIBS sparks are weaker in vacuum (see below)
- Data were taken at 3.5 m
- Laser energies 17-50 mJ
- Samples: lunar simulants and water ice (lunar poles)
- Performed multivariate analyses



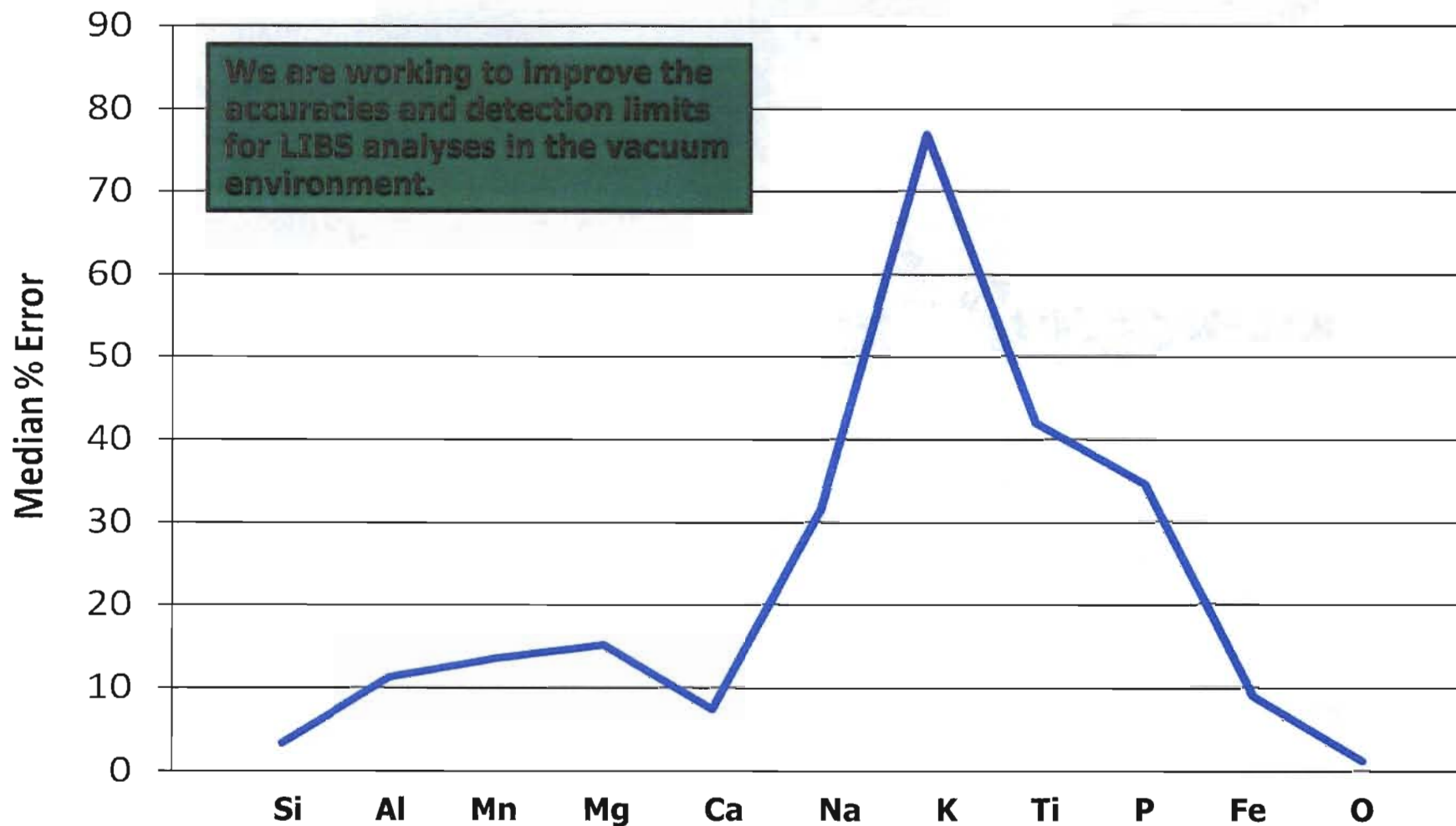
Lunar LIBS Spectra

- Significant Bremsstrahlung
- Weaker Peaks



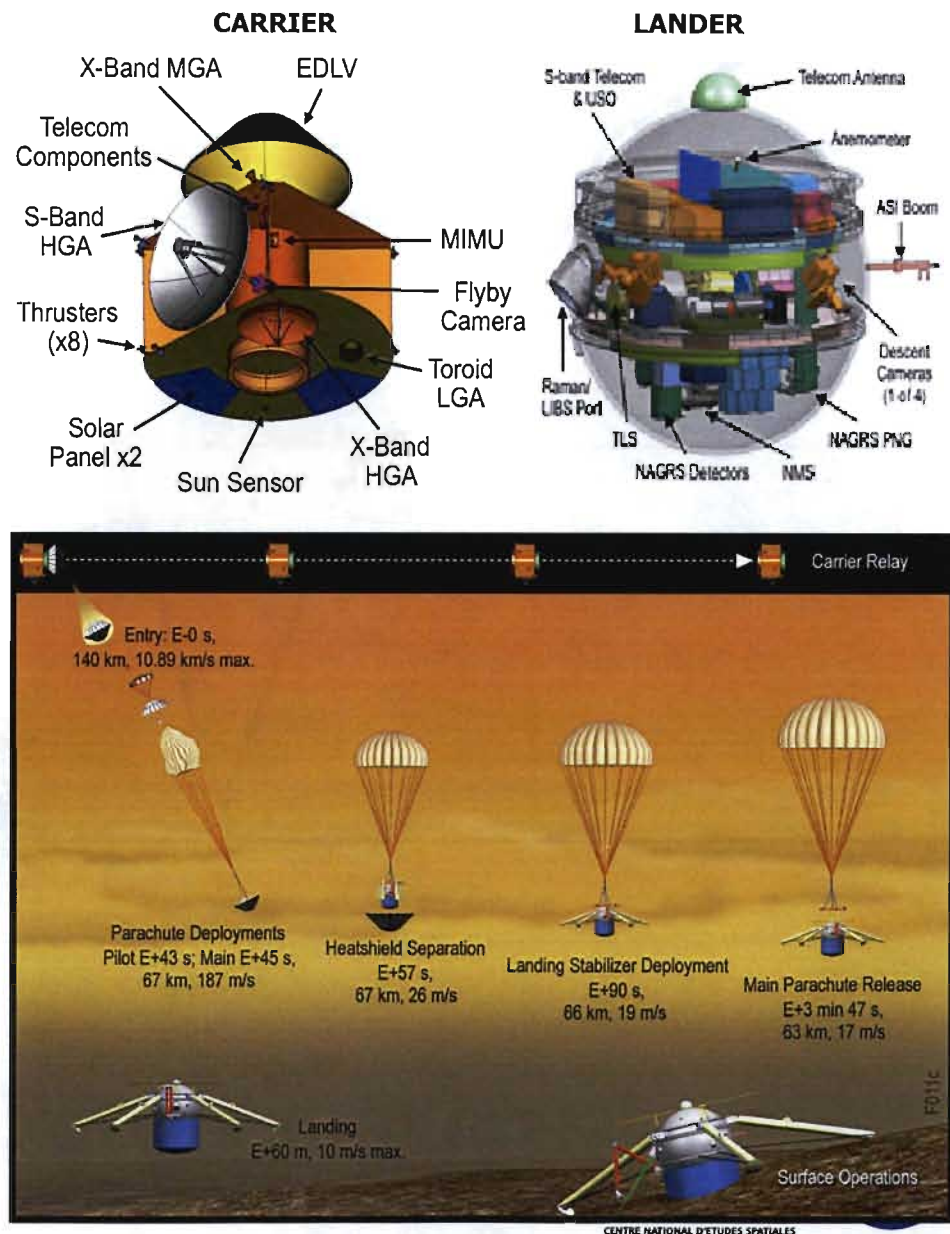
Vacuum LIBS Accuracies

17 mJ
3.5 m

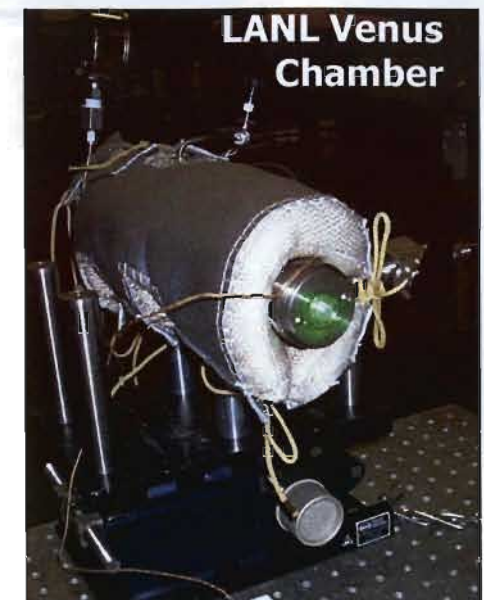
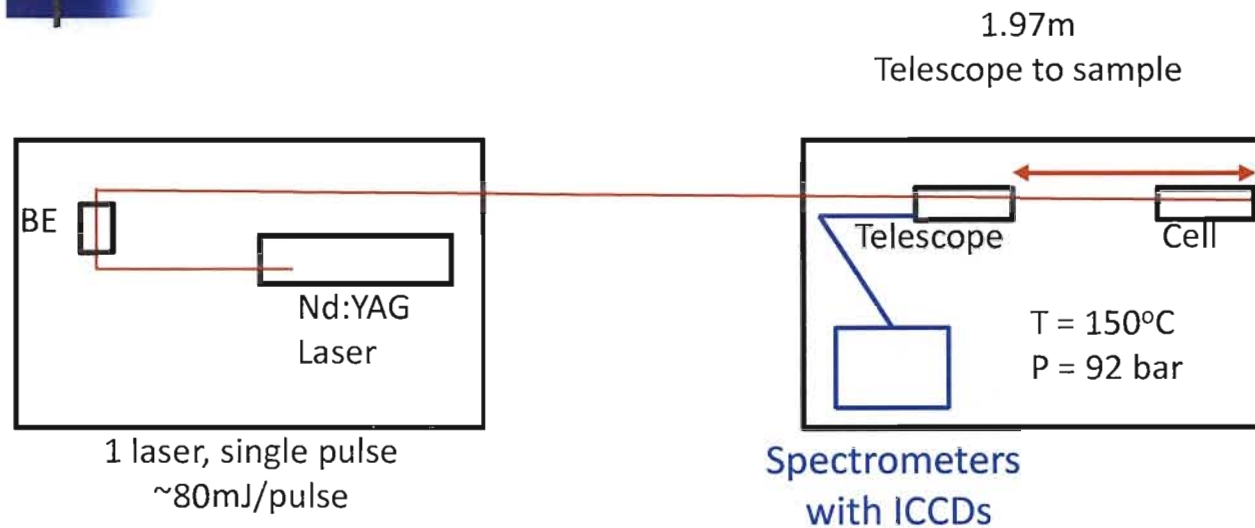


Venus Mission: SAGE*

- *Surface and Atmosphere Geochemical Observer
- May be selected next year for 2016 launch
- 3 hour surface mission, acquire high-resolution panoramic & microscopic images while performing unique elemental & mineralogical observations of the surface & subsurface.
- Instruments:
 - 3 cameras (flyby, descent & panoramic, microscopic),
 - atmospheric structure investigation,
 - 2 gas spectrometers (neutral mass, tunable laser),
 - Raman + LIBS instrument,
 - neutron-activated gamma-ray spectroscopy



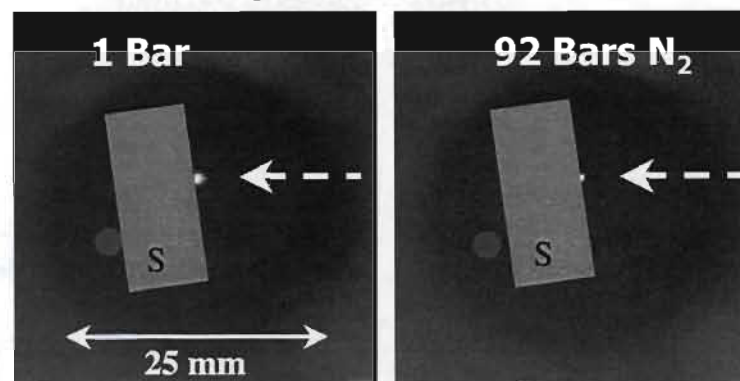
The LIBS Experiment



Stable
LIBS
Spots



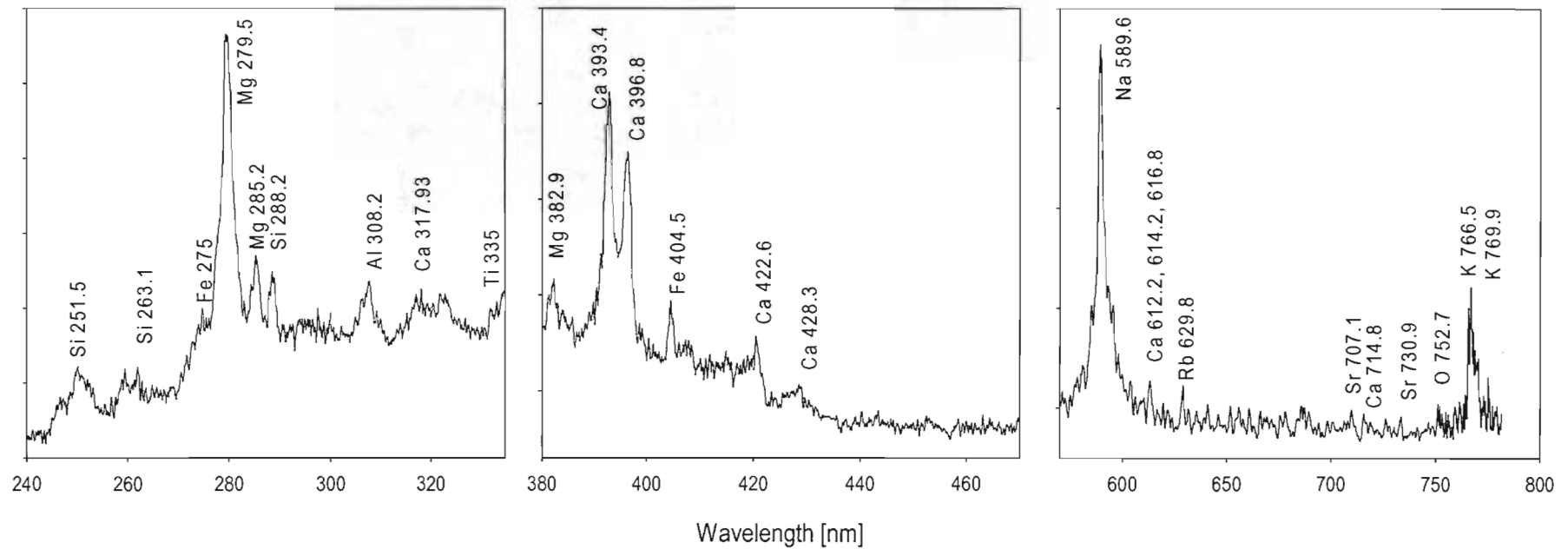
Plasma Spatial Extent



Arp et al. Spectrochim B. 59, 987, 2004.

LIBS Spectra

TAP-04 (Olivine Minette)



T 1 °C