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Title: LANL's LIBS Program

Author(s): Clegg, Samuel M.
Wiens, Roger C.
Barefield, James E.

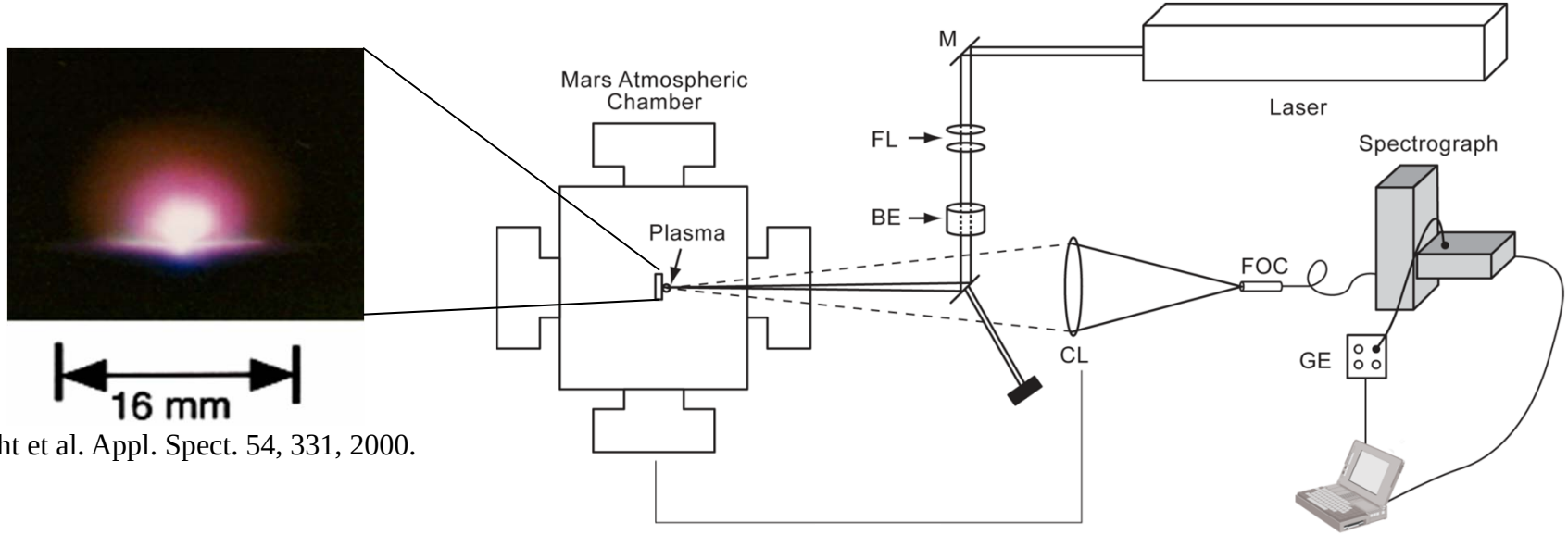
Intended for: Program Meeting at PNNL

LANL's LIBS Program

Samuel M. Clegg, James E. Barefield and Roger C. Wiens

Laser Induced Breakdown Spectroscopy (LIBS)

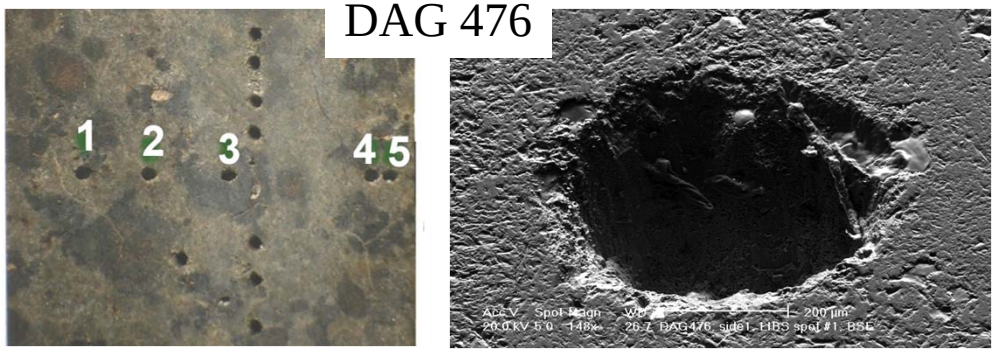
LIBS 1064 nm, Raman 532 nm



Knight et al. Appl. Spect. 54, 331, 2000.

9.0m

DAG 476

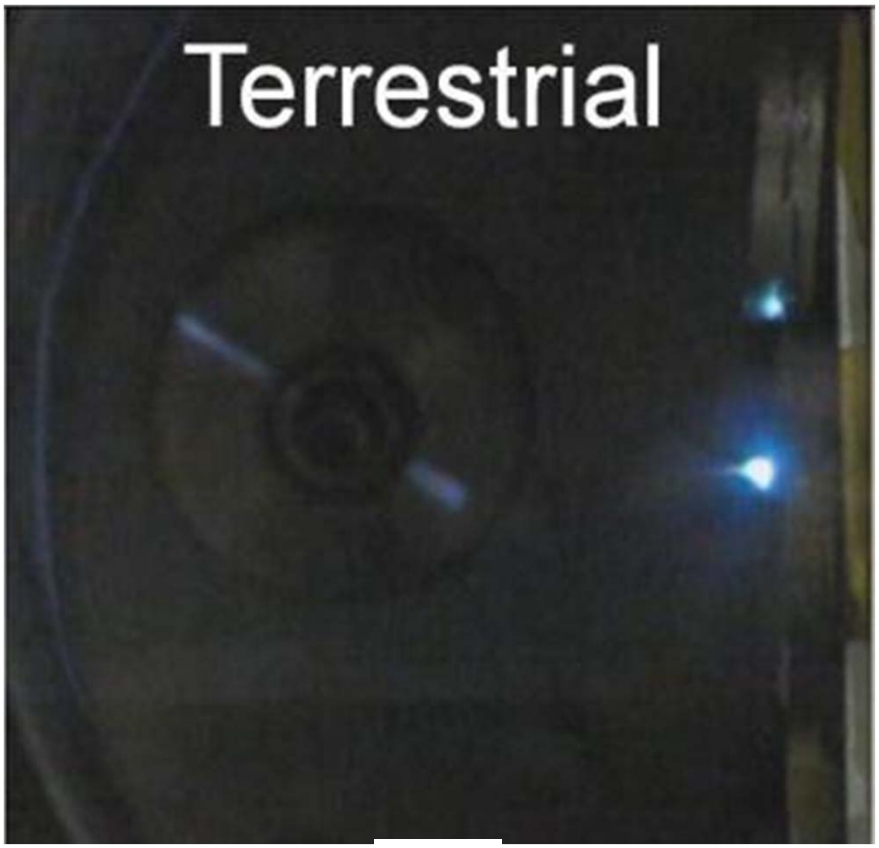


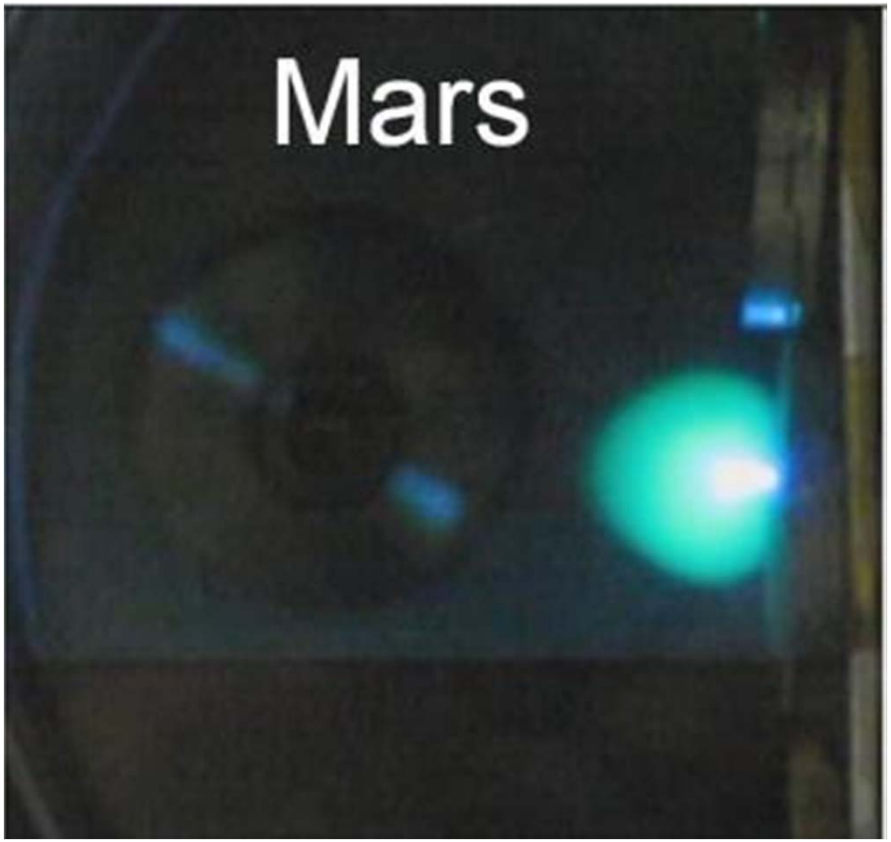
Thompson et al. JGR-P 111 E05006 2006.

200μm

What Really Happens?

What Really Happens!



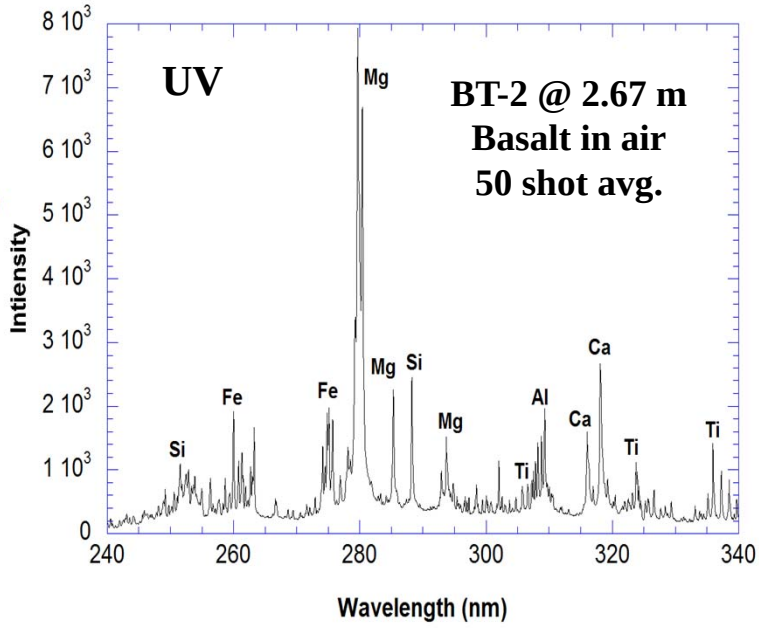


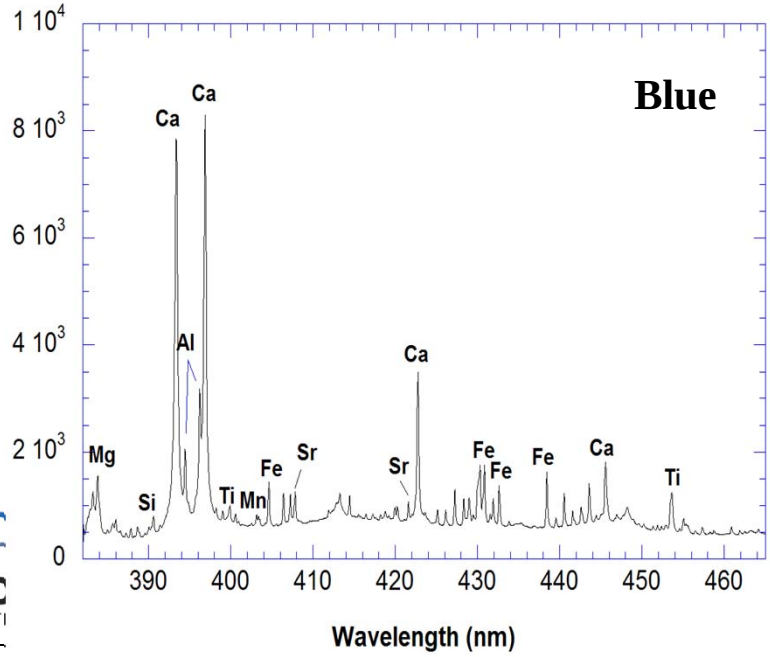
3”

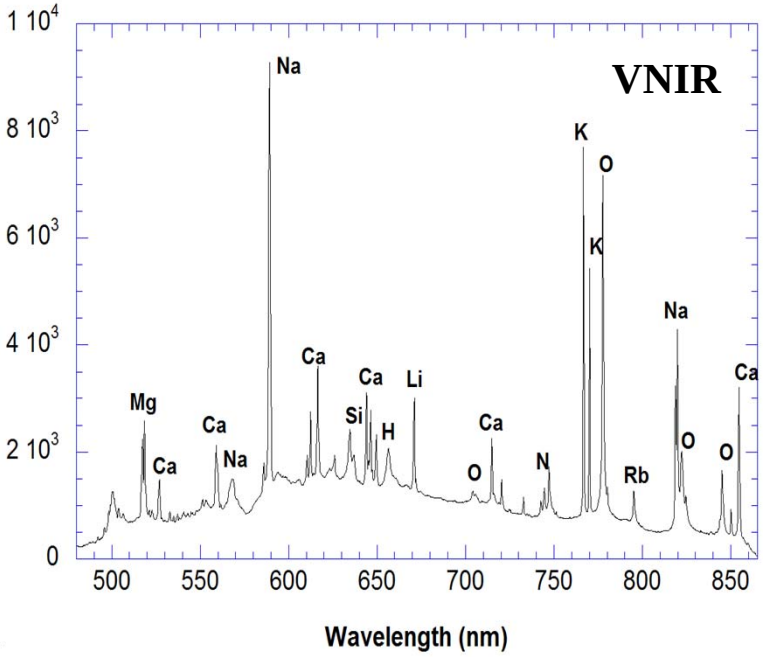
ChemCam FM Spectra

Three Spectrometers
Similar to Ocean Optics HR2000

For ChemCam,
Sony CCD replaced with e2v CCD
Non-Linearity Resolved







LANL LIBS Carbon Sequestration Program

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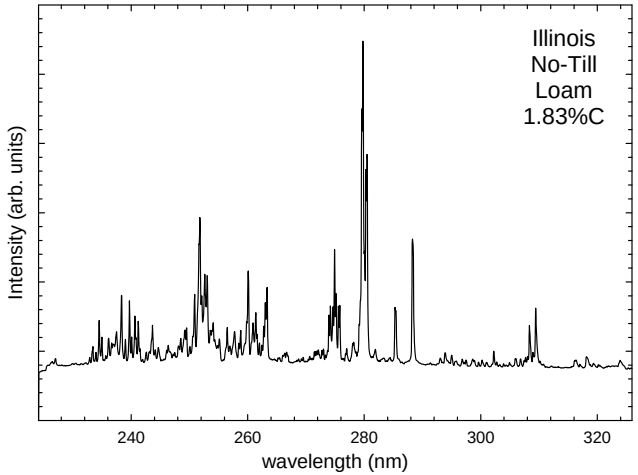
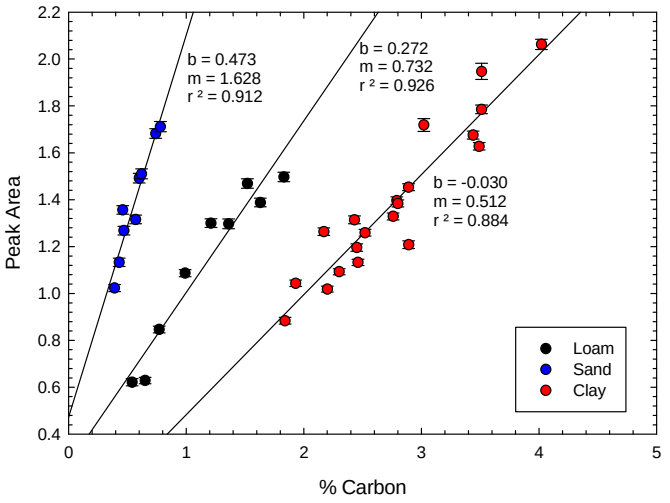
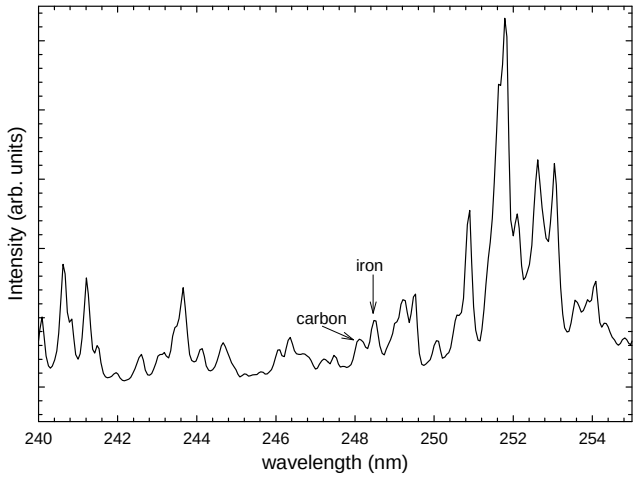
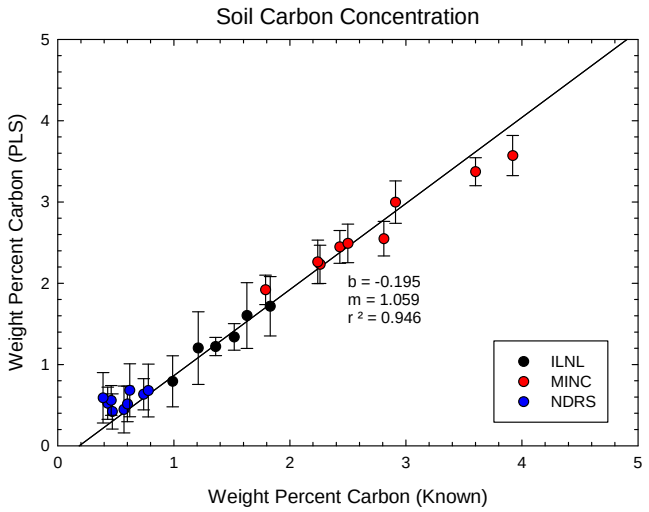
In Situ Detection of Carbon & Multivariate Analysis









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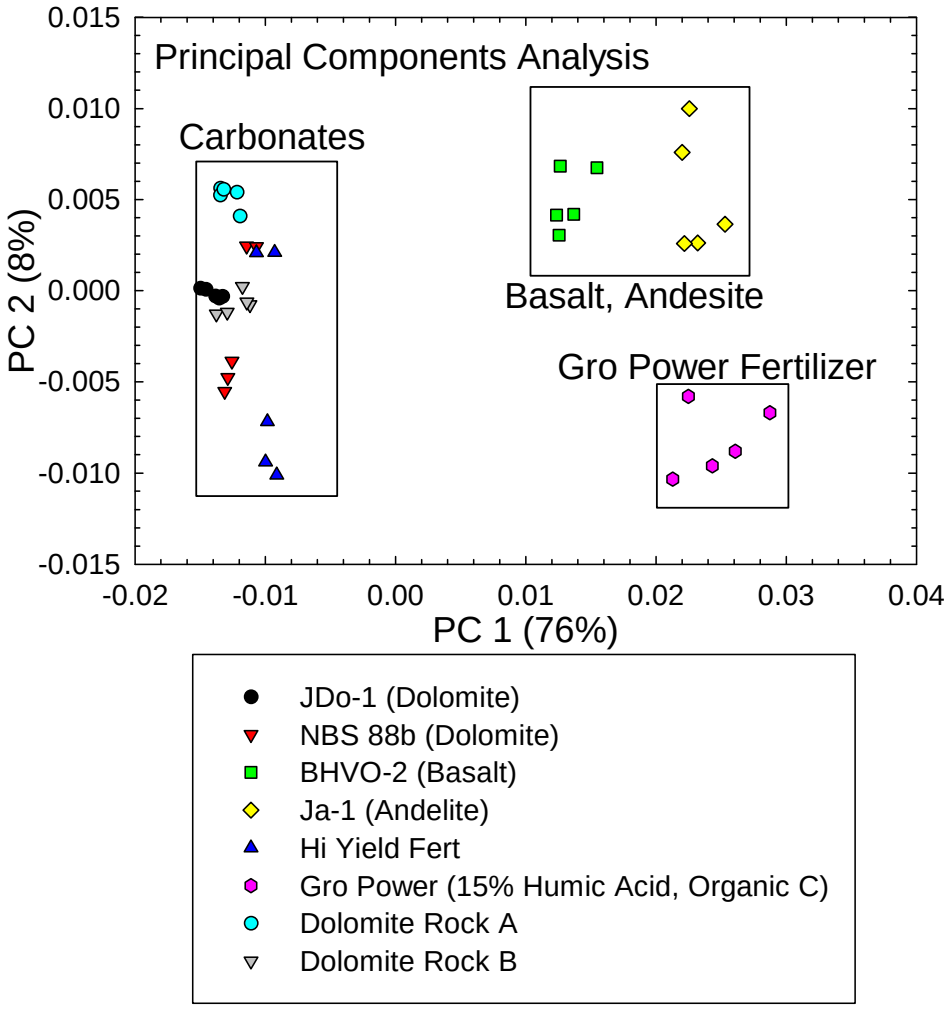
Organic vs. Inorganic Samples



LANL LIBS Actinide Detection Programs

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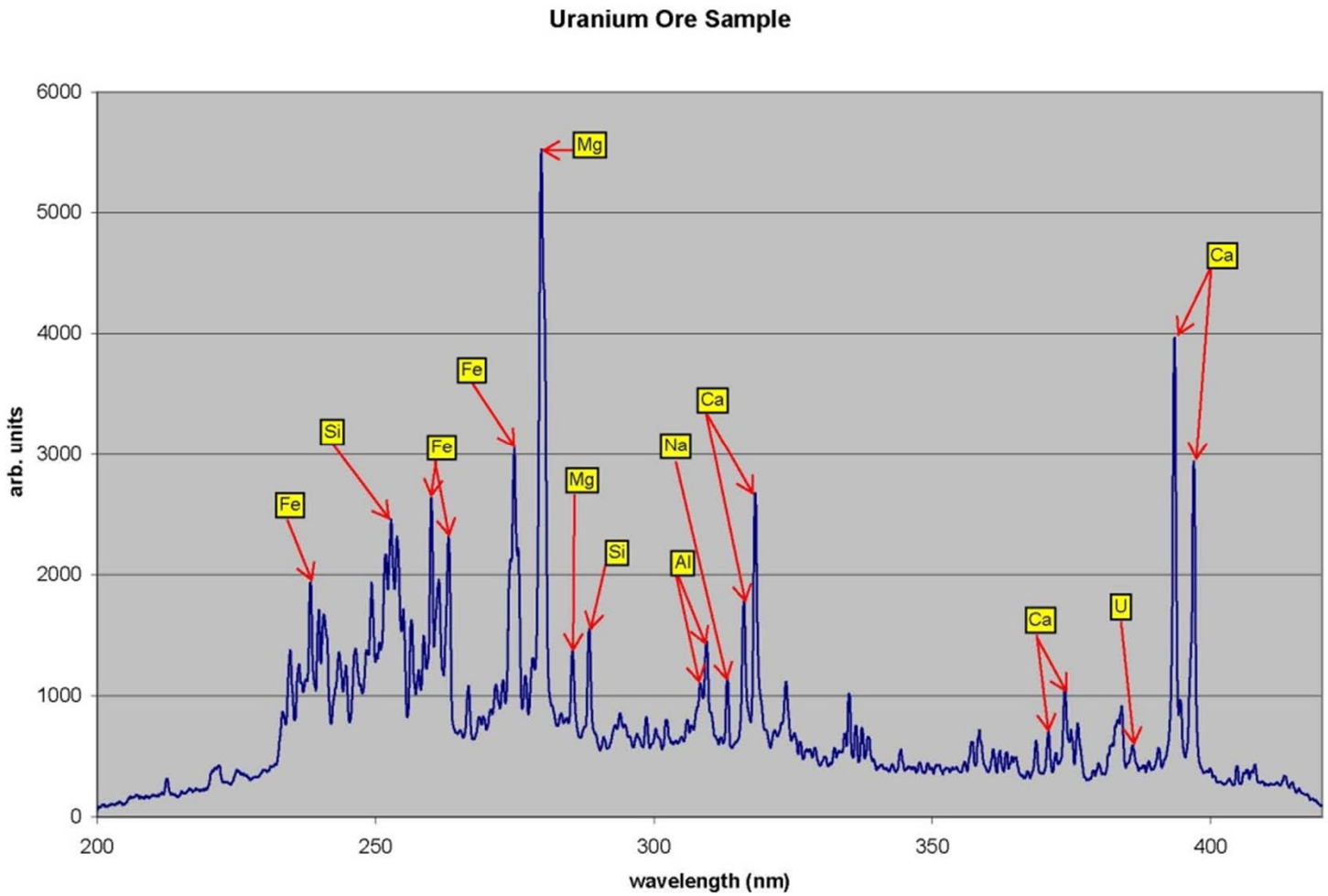
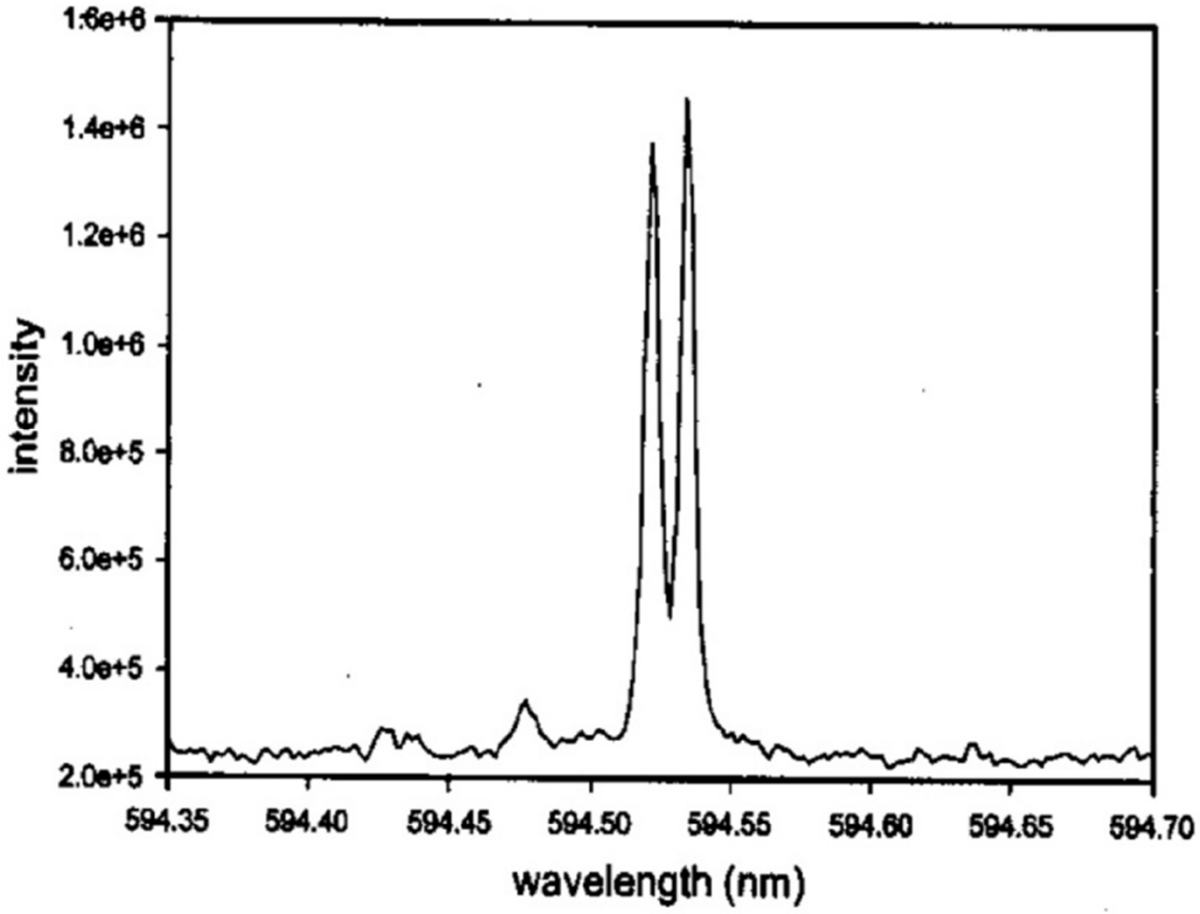
LIBS Backpack Mounted System

Uranium Ore sample



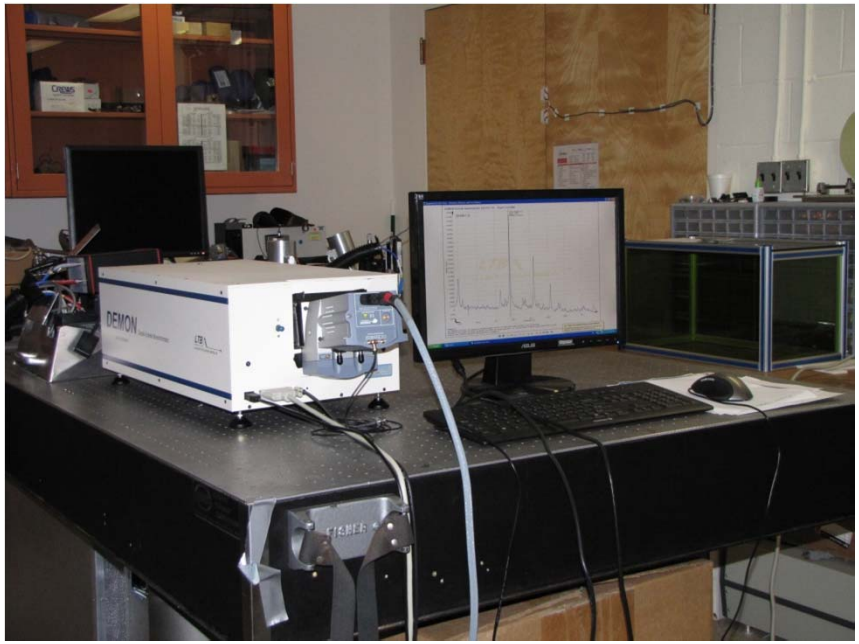
High Resolution LIBS Raman System LANL

Pu Isotopic Ratio - Pu(239) / Pu(240) 49:51

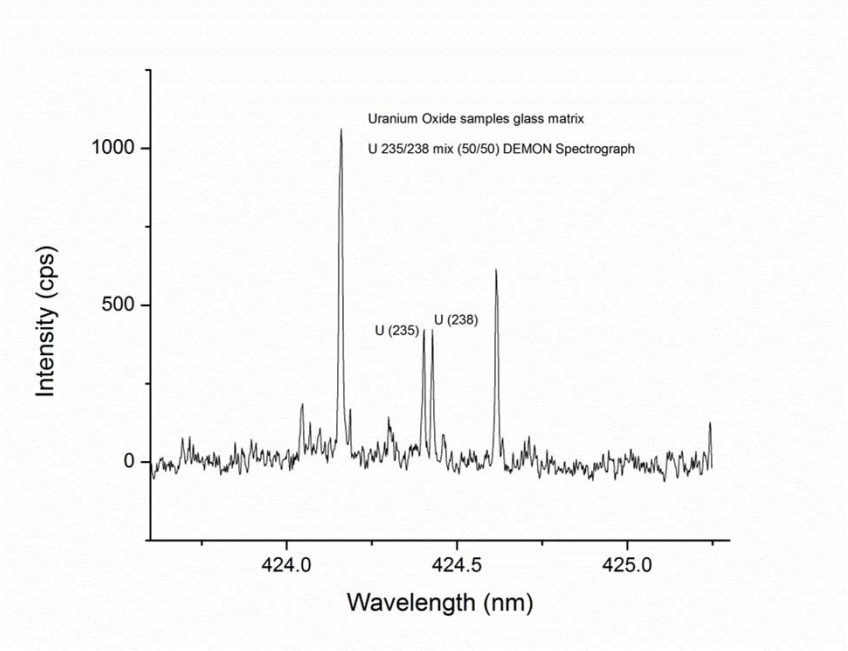


High Resolution LIBS system with Isotopic Sensitivity for U and Pu

High Resolution LIBS System (res ~75,000) Pu and U isotopics

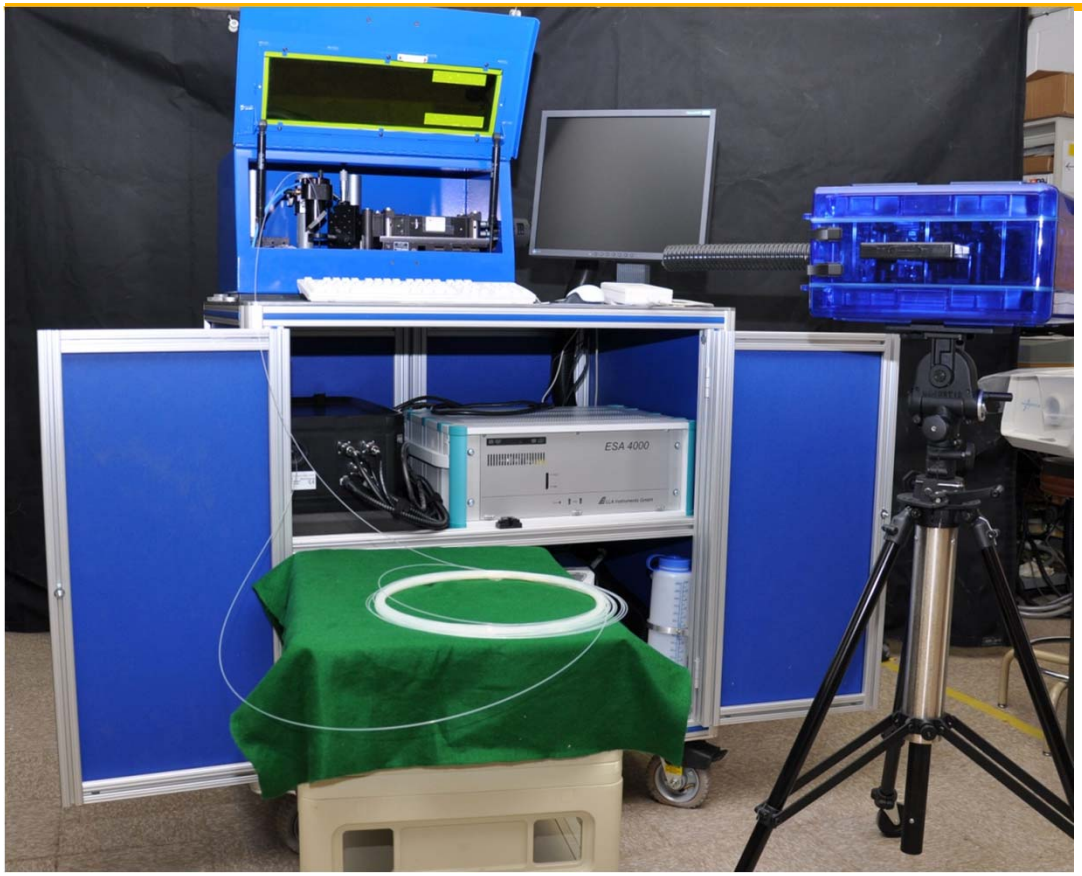


Uranium Oxide in Glass matrix 50/50 U (235/238)

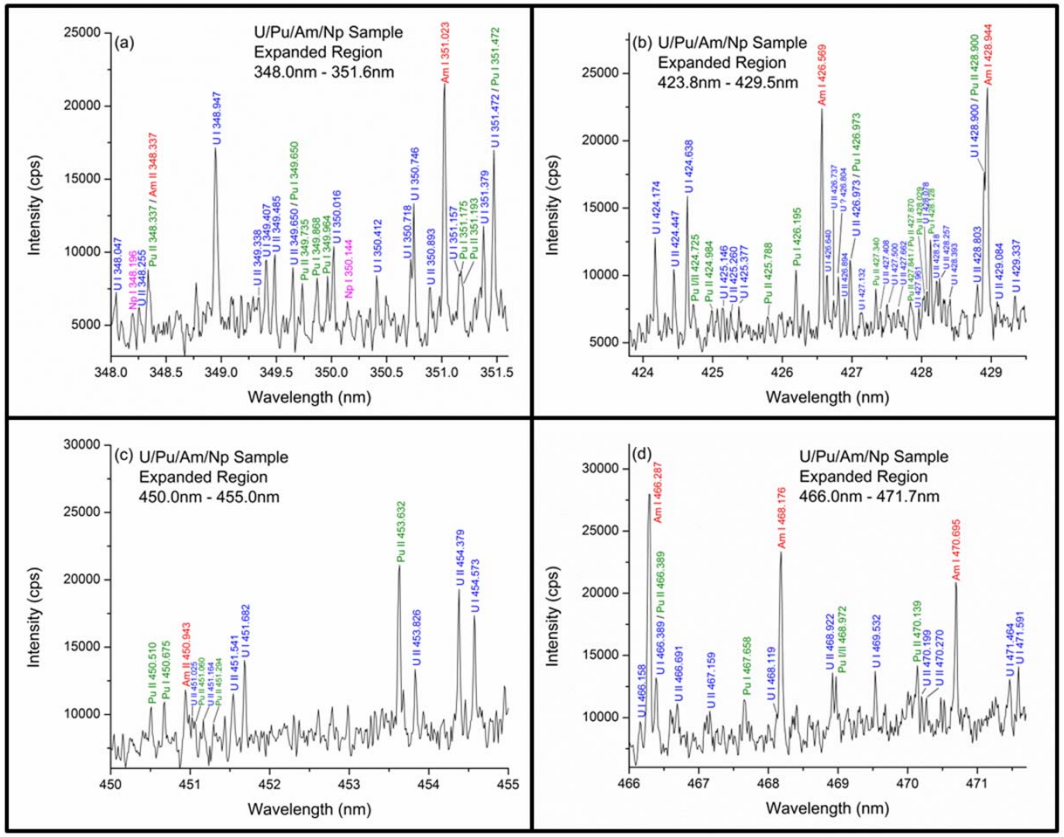


Rack / Cart Mounted LIBS System

Medium Res. LIBS System ~20,000 (λ/Δλ)



Medium Res. (~20,000) LIBS Spectra of Mixed Actinide Oxides Samples U / Pu / Am / Np



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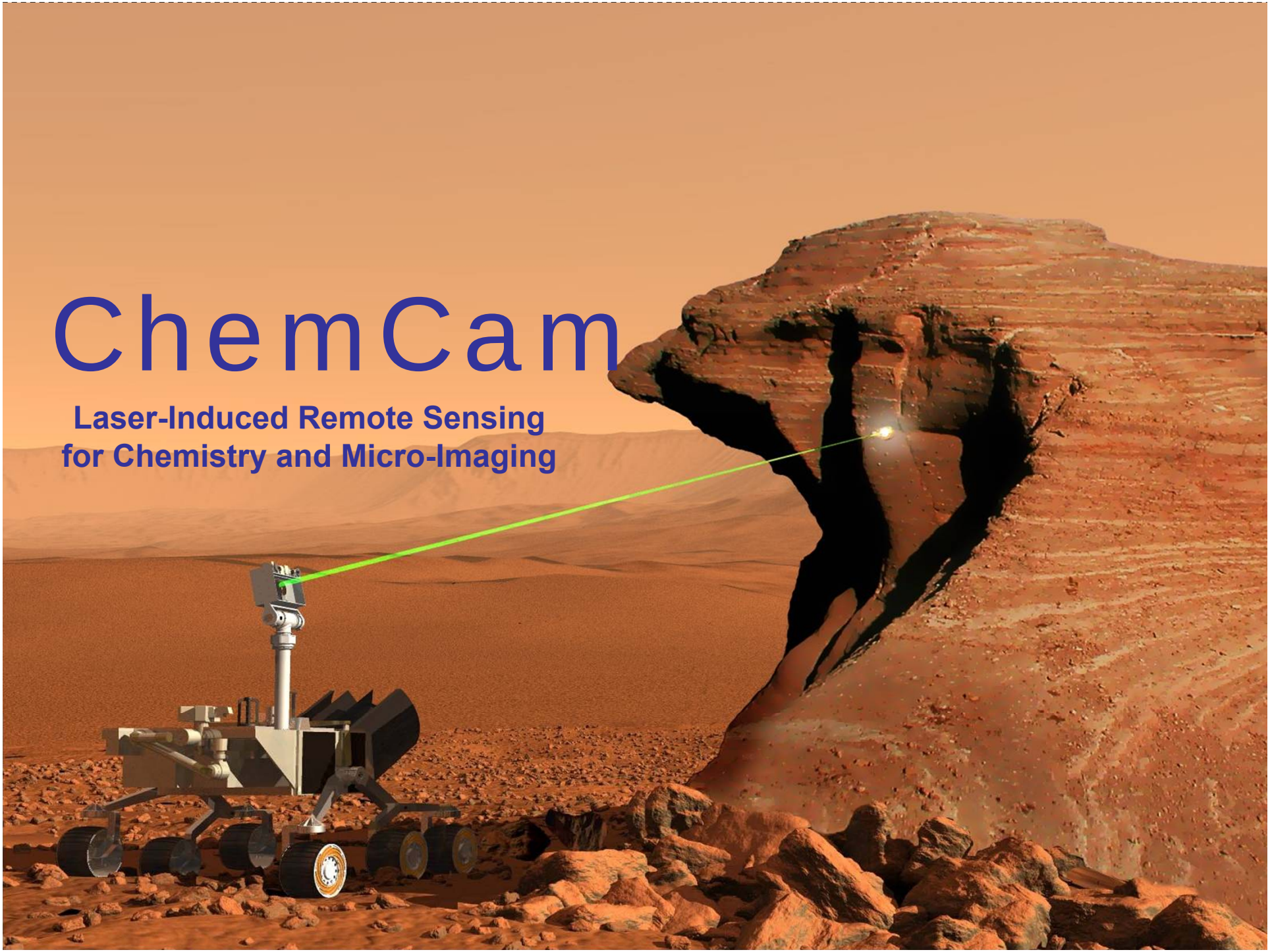
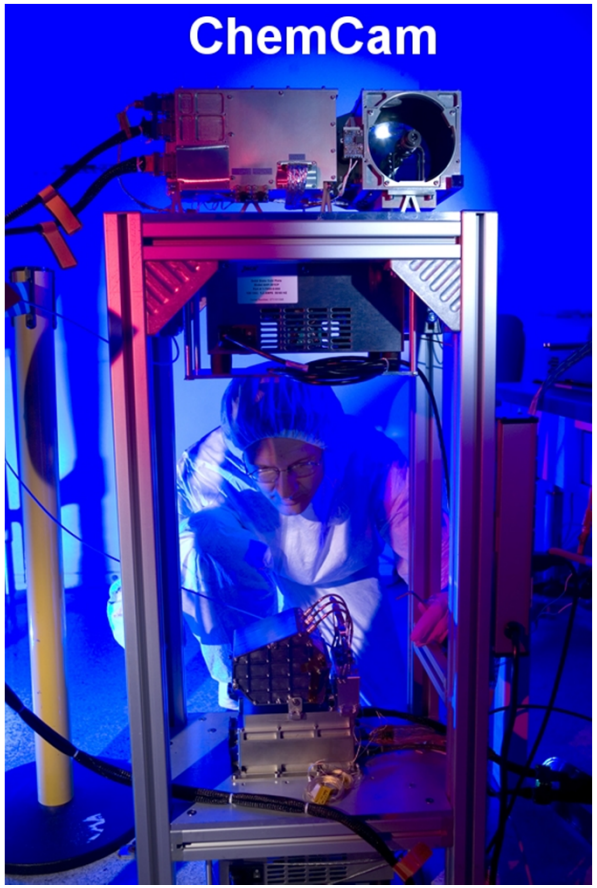
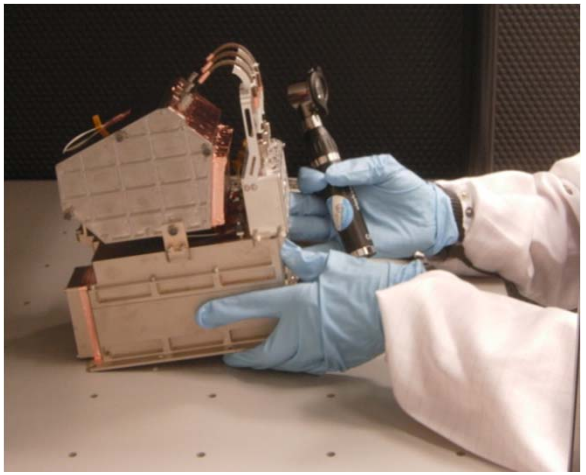
ChemCam

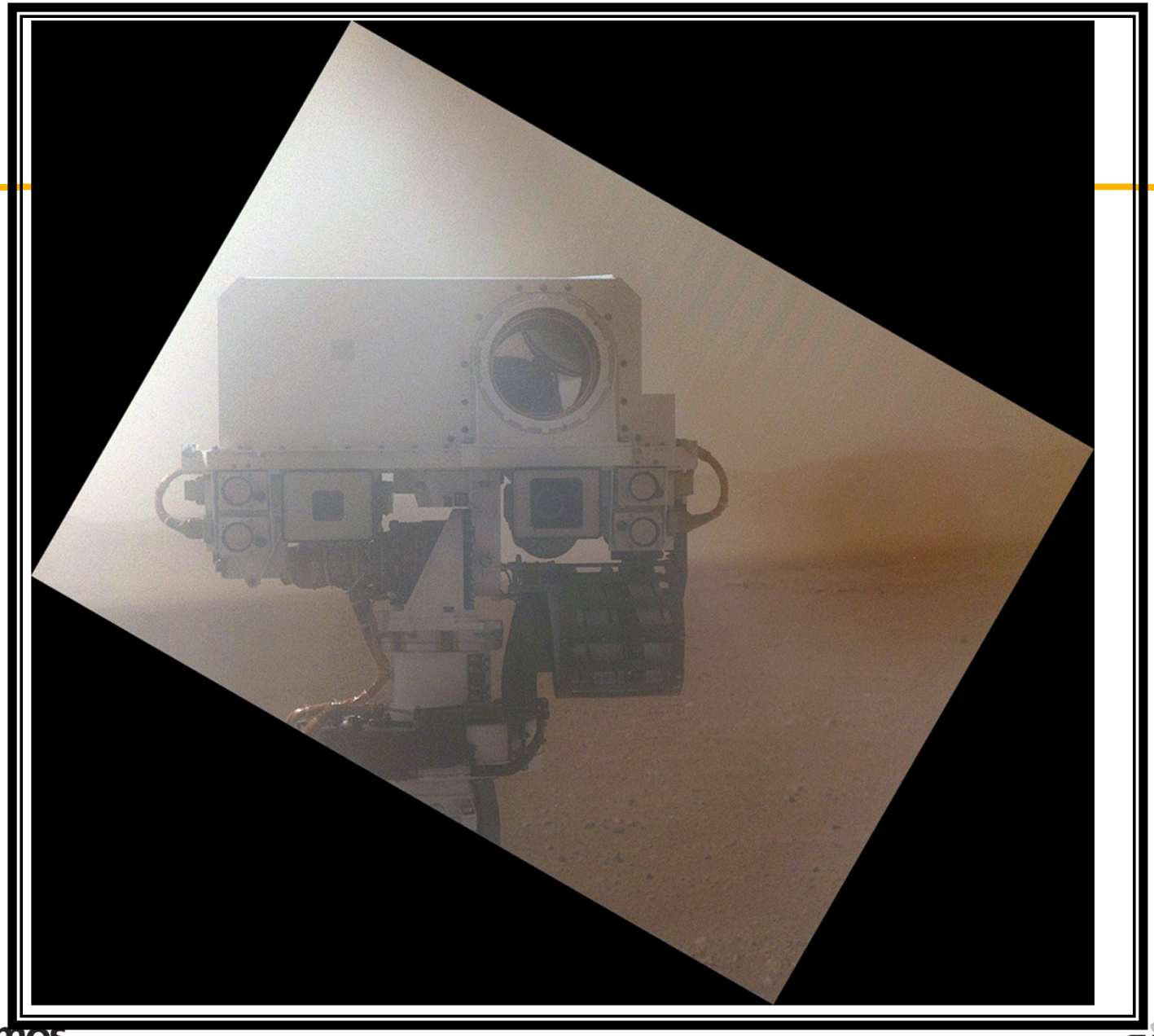
Laser-Induced Remote Sensing for Chemistry and Micro-Imaging



ChemCam Engineering Model







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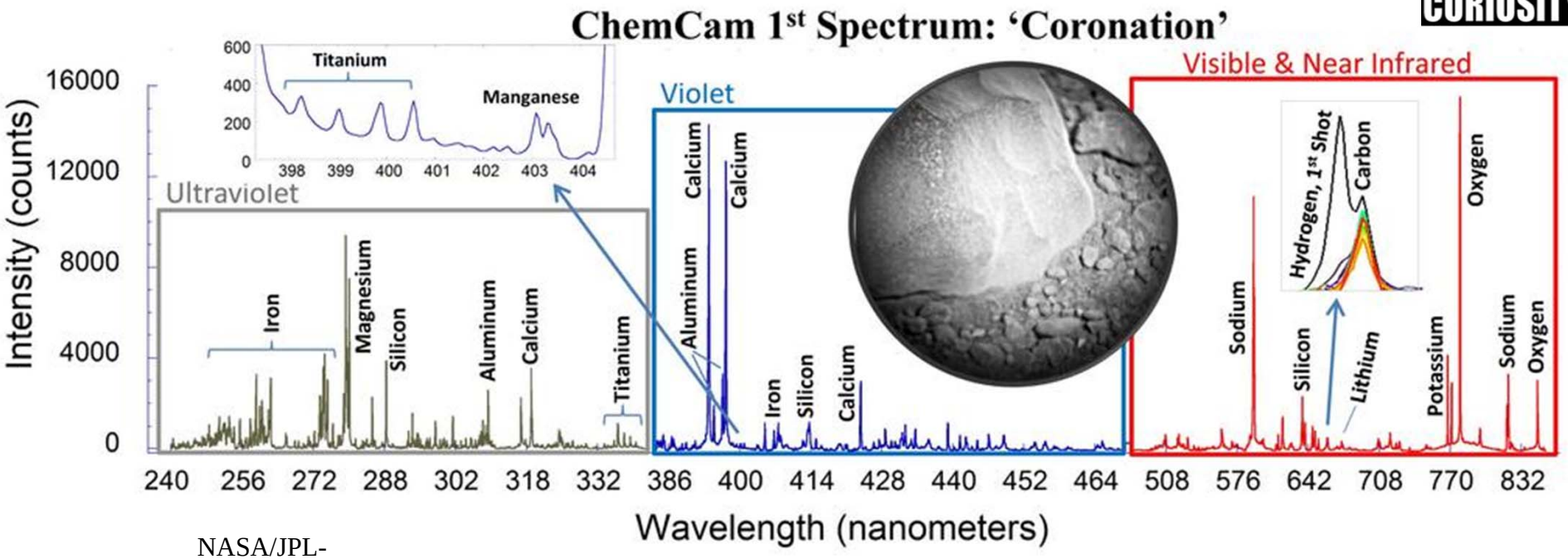
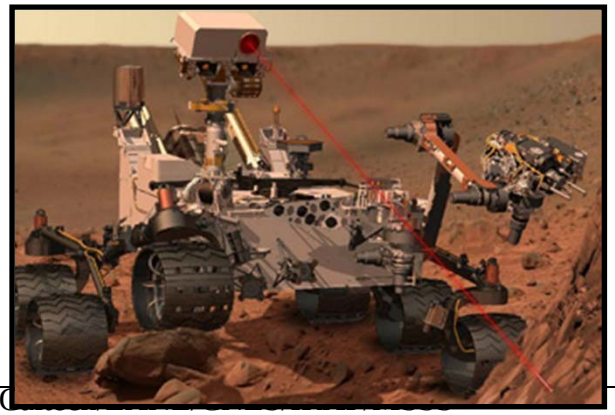
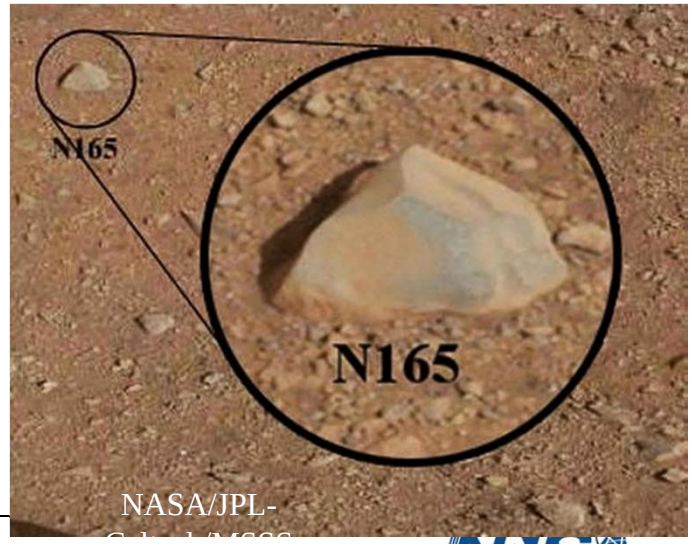


NASA/JPL-
Caltech/LANL/CNES/IRAP/MSSS

ChemCam spectra of Coronation

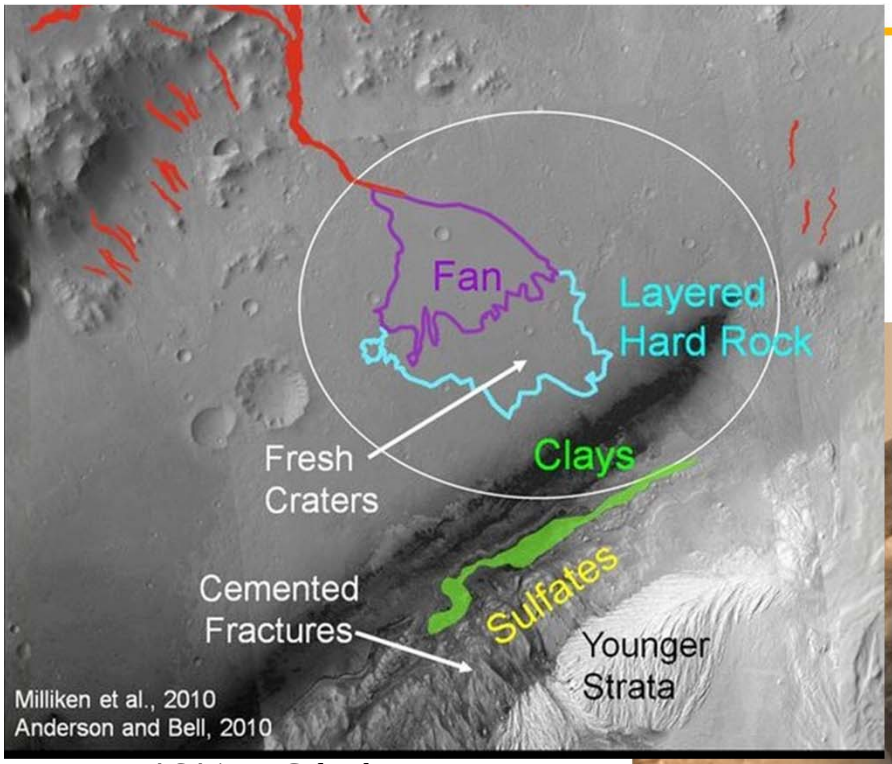
Target: Coronation (N165)
Sol 13
Shots: 30



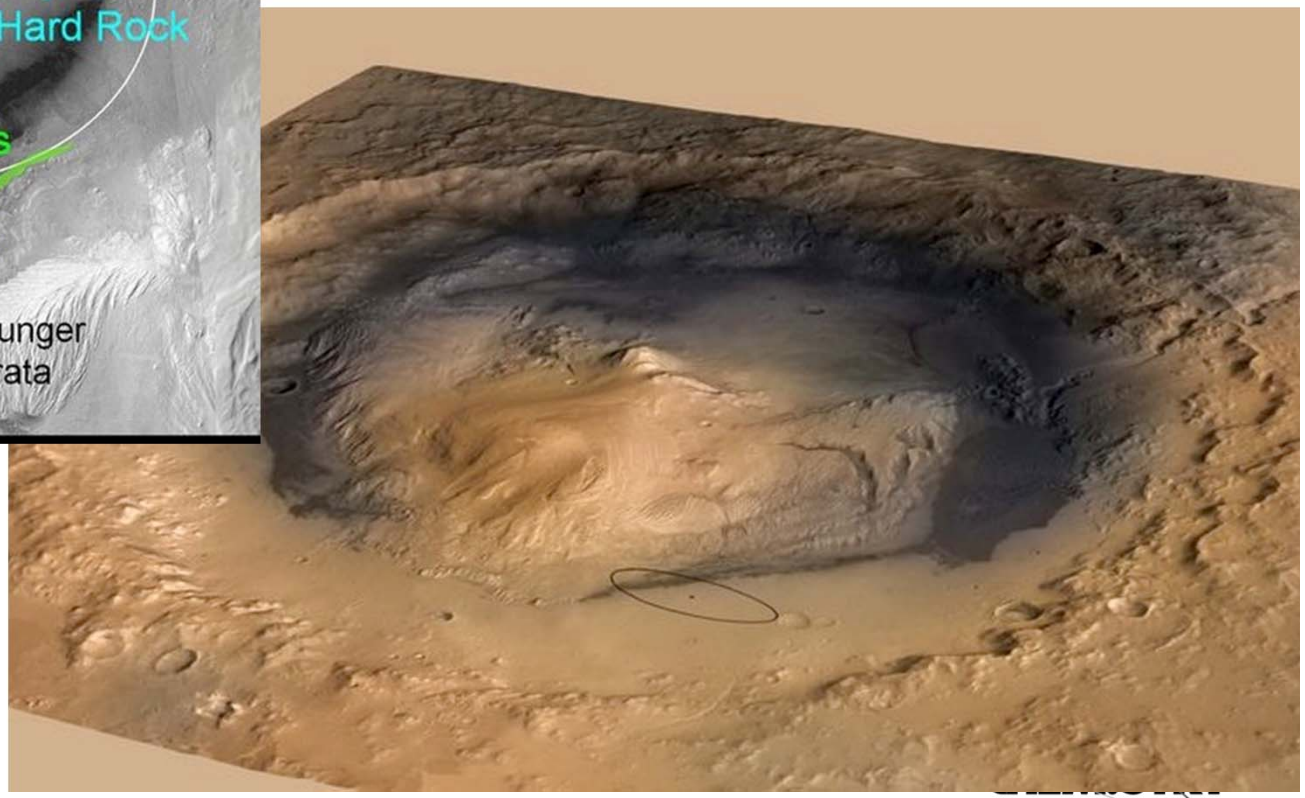


NASA/JPL-

Target: Gale Crater and Mount Sharp



NASA/JPL-Caltech



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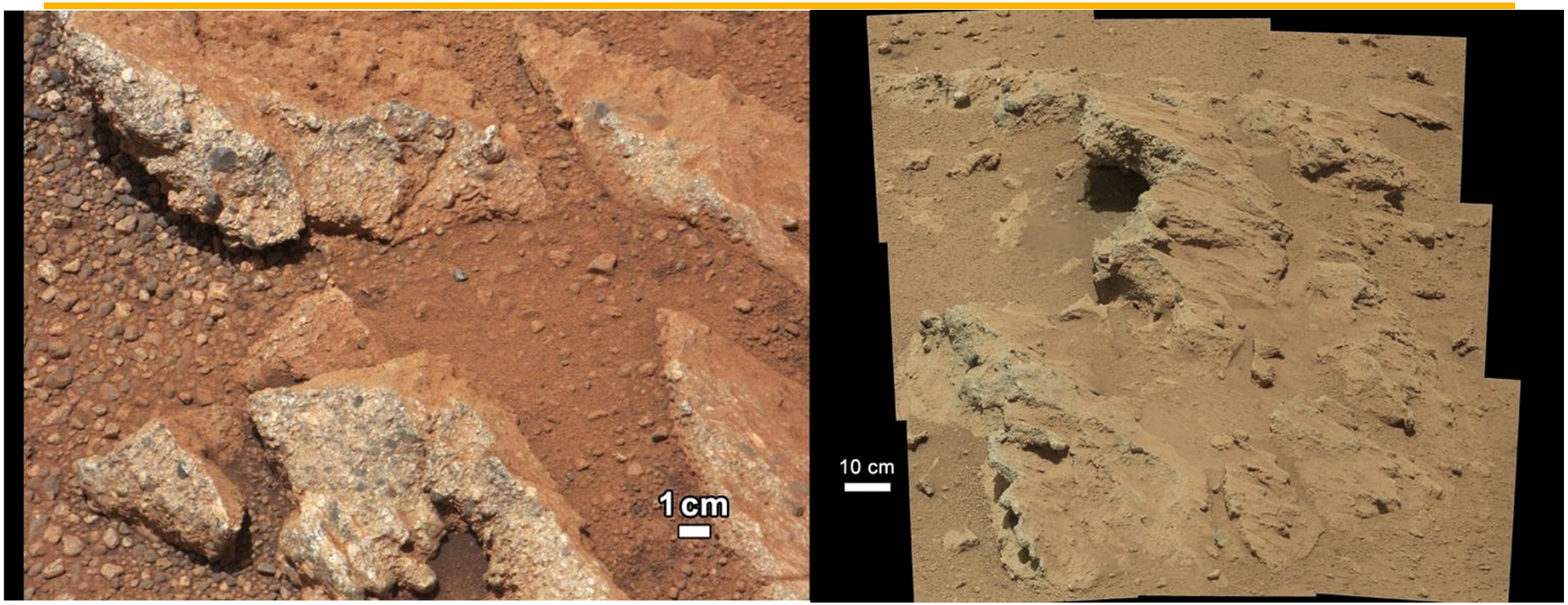
ChemCam Mosaic, Goulburn Scour

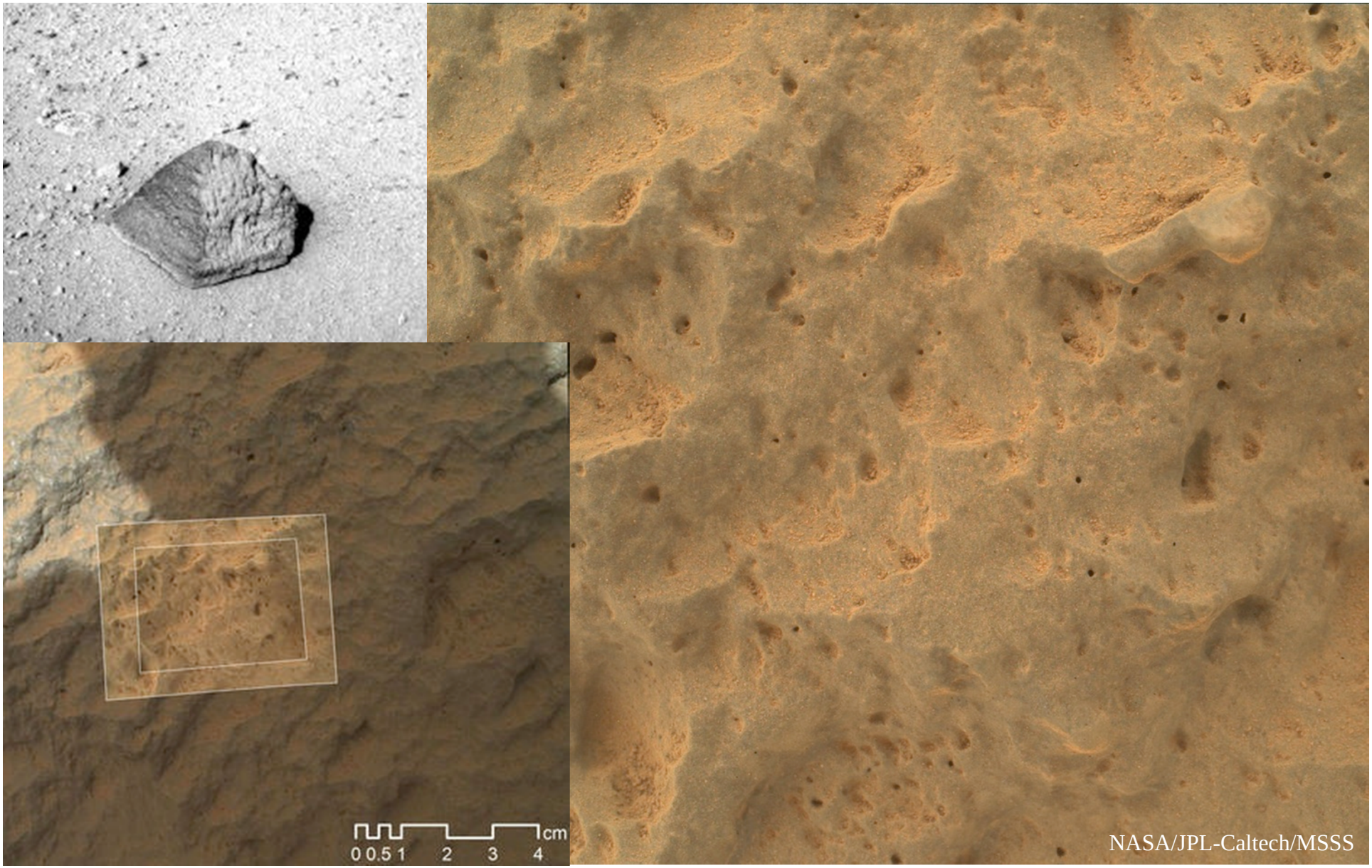
ChemCam RMI mosaic of small outcrop exposed by the sky crane thrusters

Scale of RMI images: ~10 cm dia
Distance: 5-6 m

NASA/JPL/LANL/IRAP/CNES/MSSS/LTMP


1 cm
10 cm

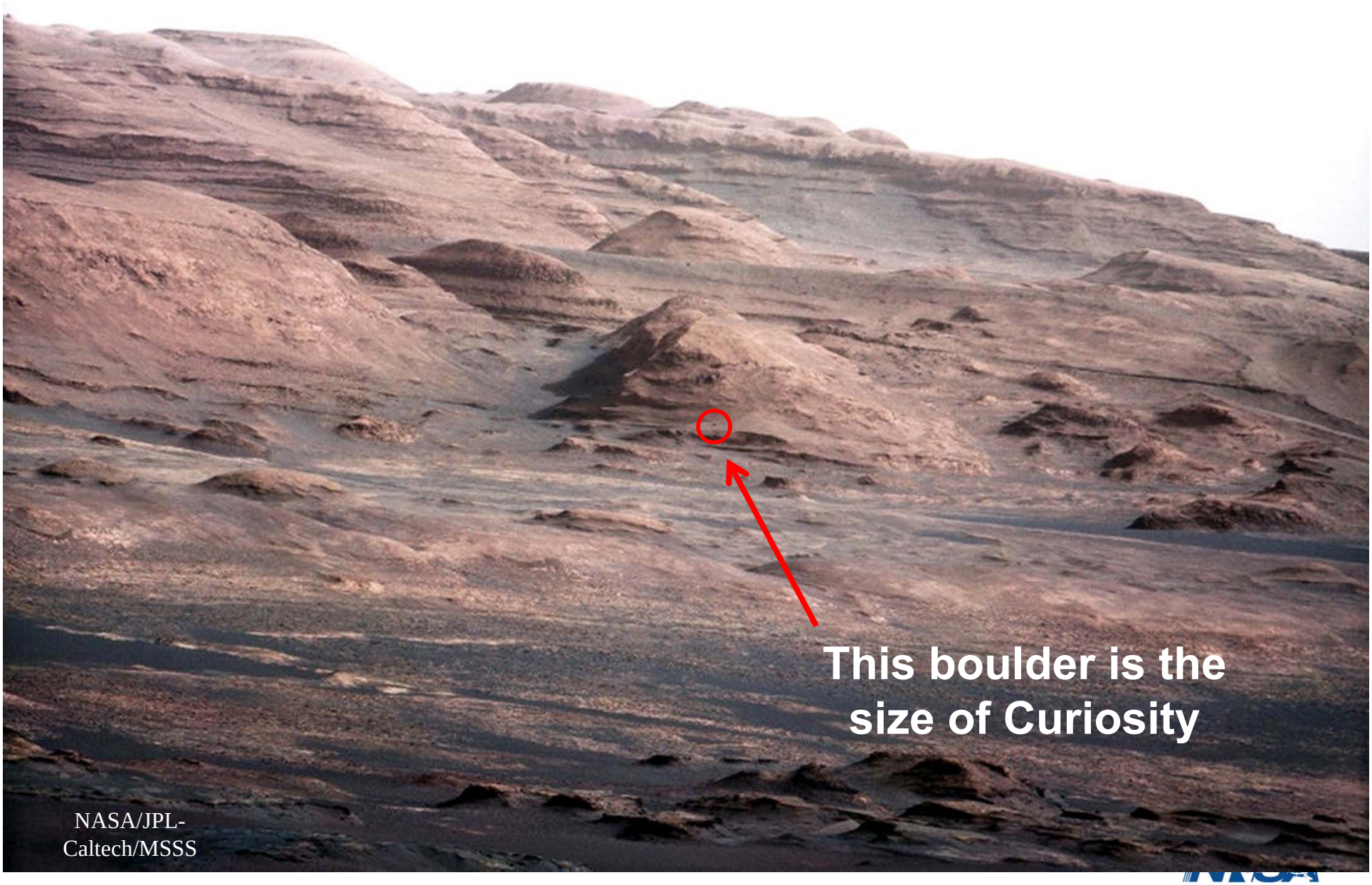
Nested, hand-lens imaging of the 25-cm (10”) high rock Jake Matijevic



Beechey Soil Raster

Distance 3.5 m
Field of view 8 cm
50 shots each hole
Images slightly offset
Distance between holes ~3.5 mm

Mastcam-100 image of Mount Sharp's layers, canyons and buttes



NASA/JPL-Caltech/MSSS

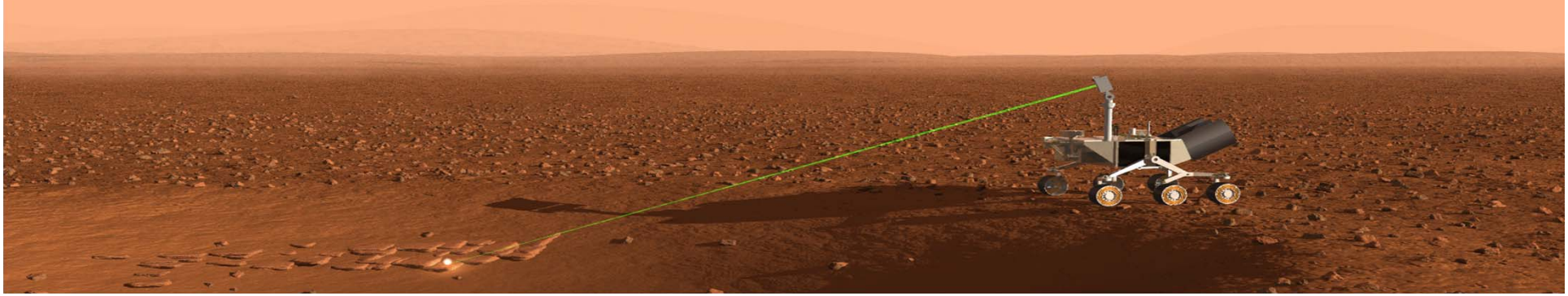
LIBS Quantitative Elemental Analysis

Multivariate Analysis

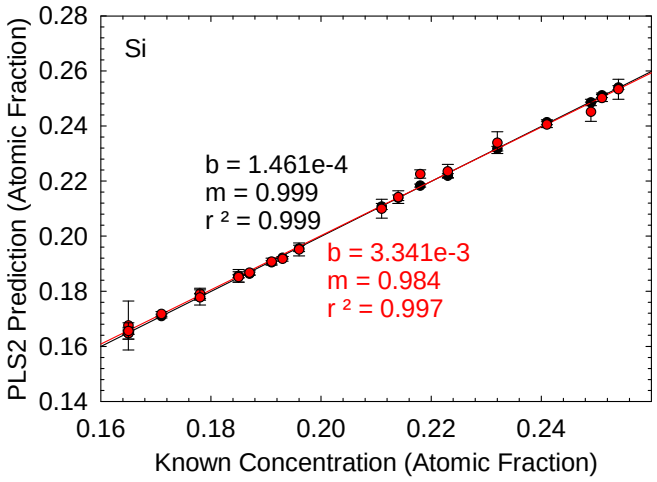
Partial Least Squares (PLS)

Principal Components Analysis (PCA)

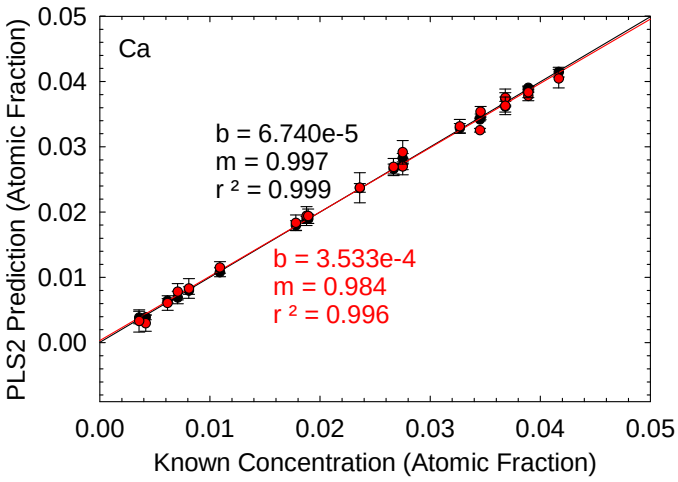
Independent Components Analysis (ICA)

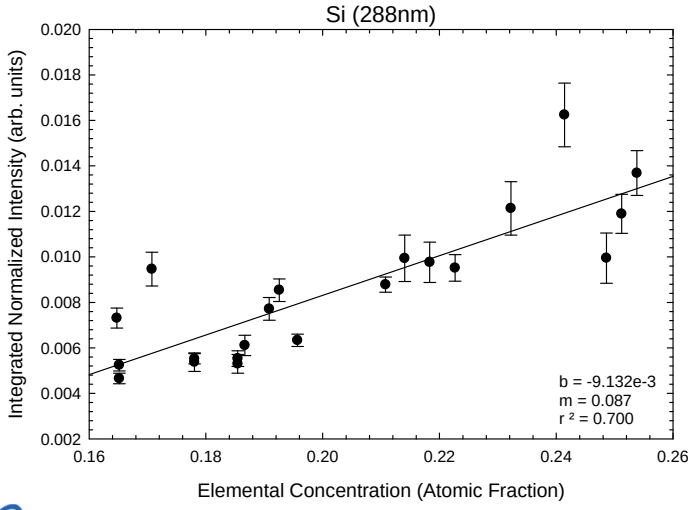


PLS vs. Peak Area

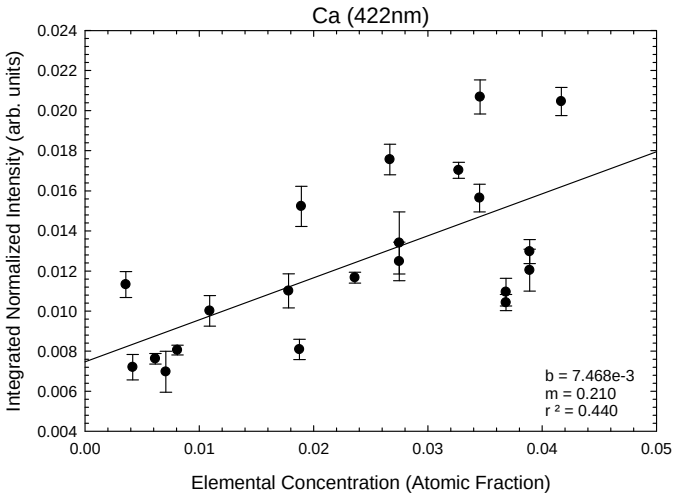


PLS





Peak Area



● Calibration ● Validation

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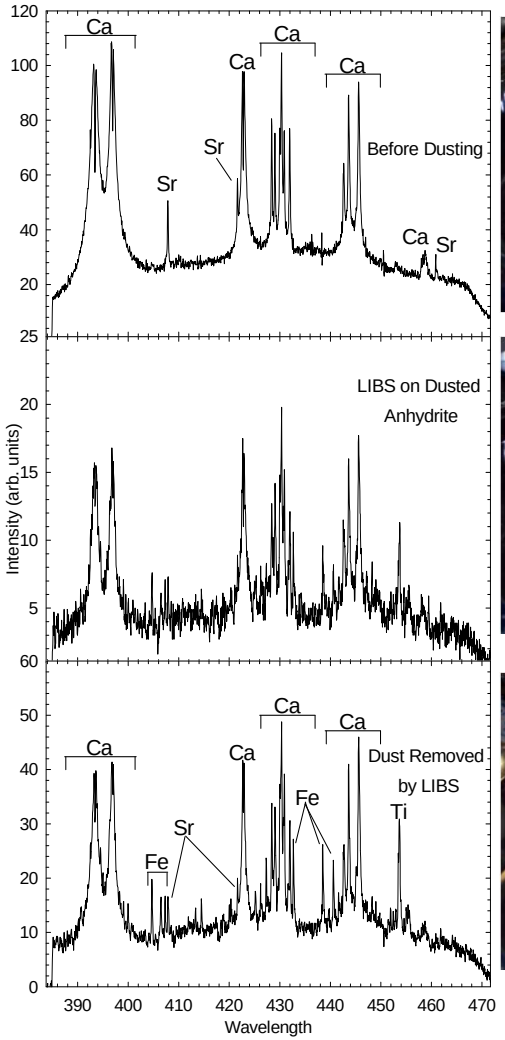
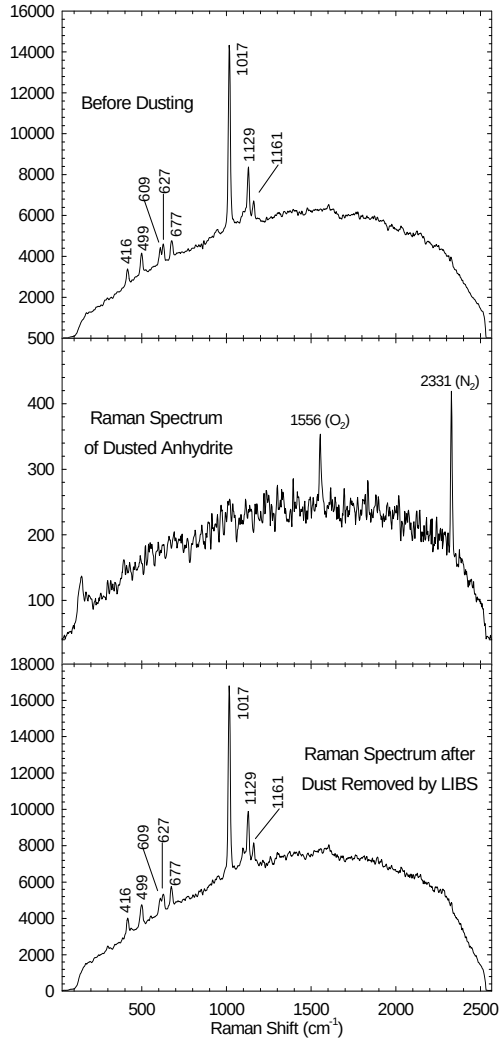
Remote Raman – LIBS on the Venus Surface and Atmosphere Geochemical Explorer (SAGE)

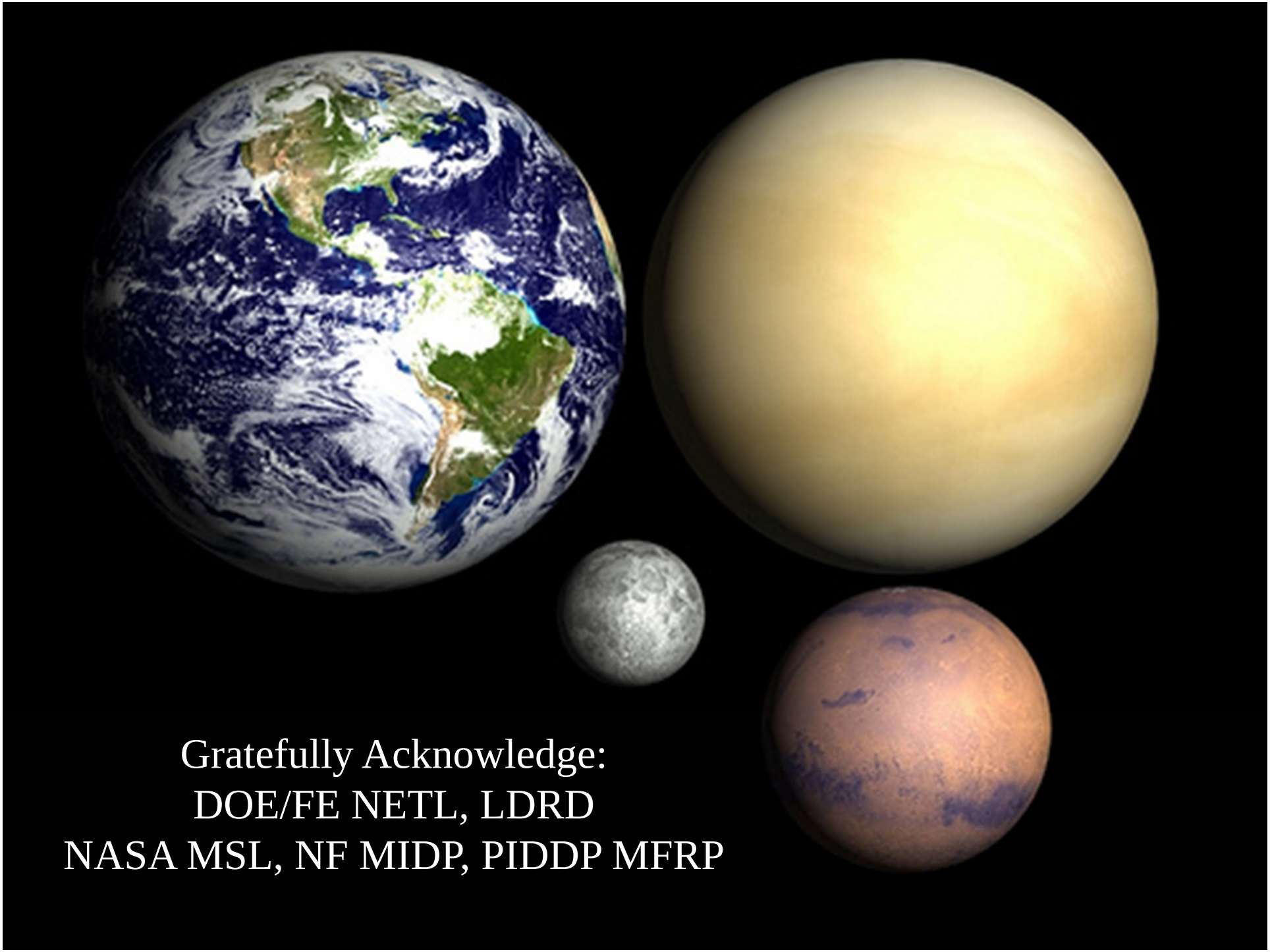
Raman – LIBS
Solves Raman Limitations

LIBS

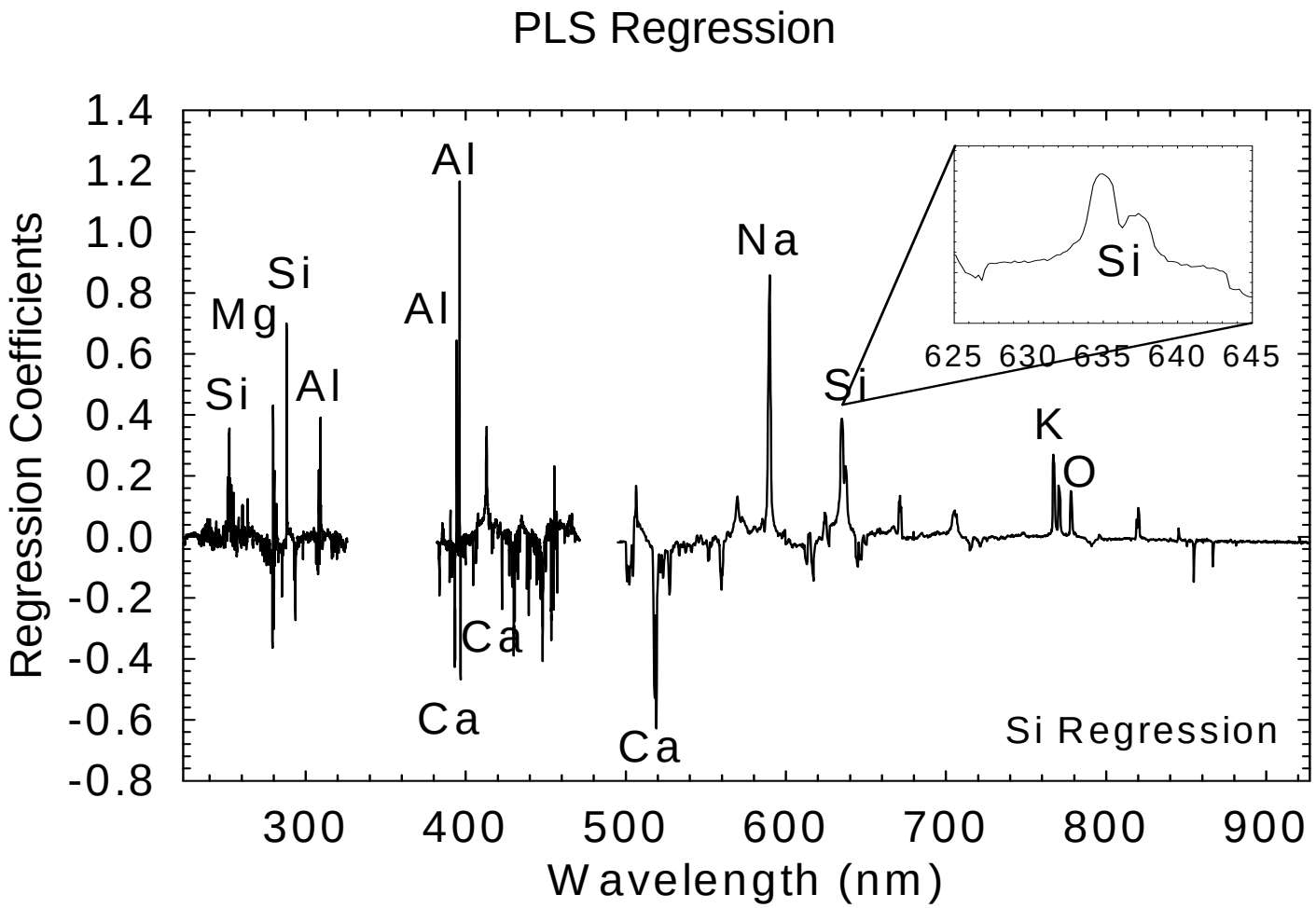


Raman




Gratefully Acknowledge:
DOE/FE NETL, LDRD
NASA MSL, NF MIDP, PIDDP MFRP

New Multivariate Analysis Techniques
Partial Least Squares (PLS)



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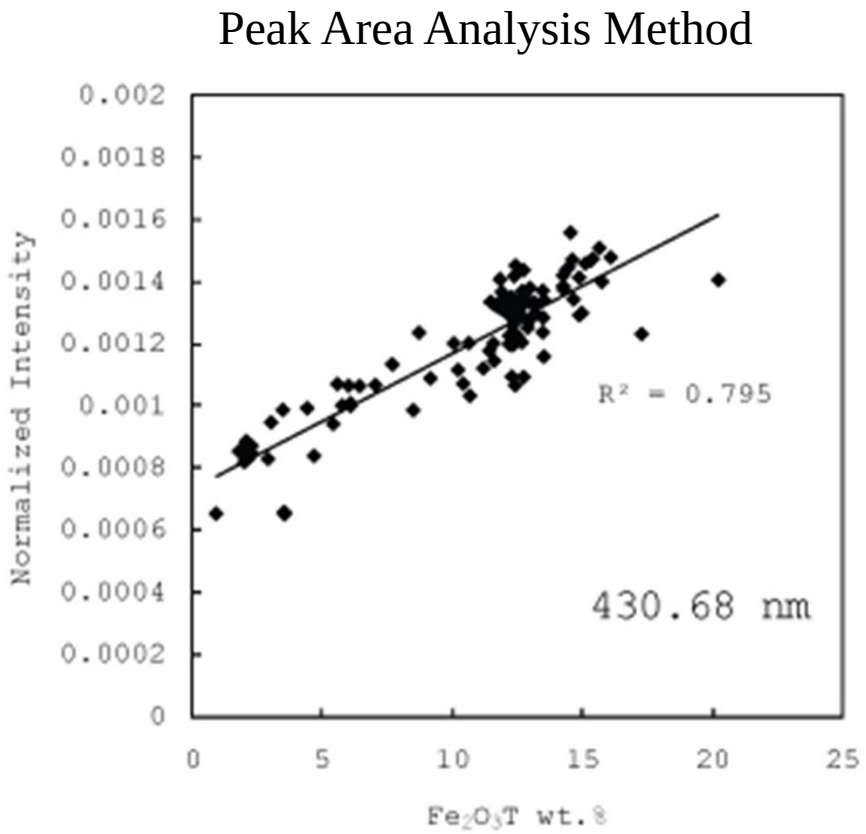
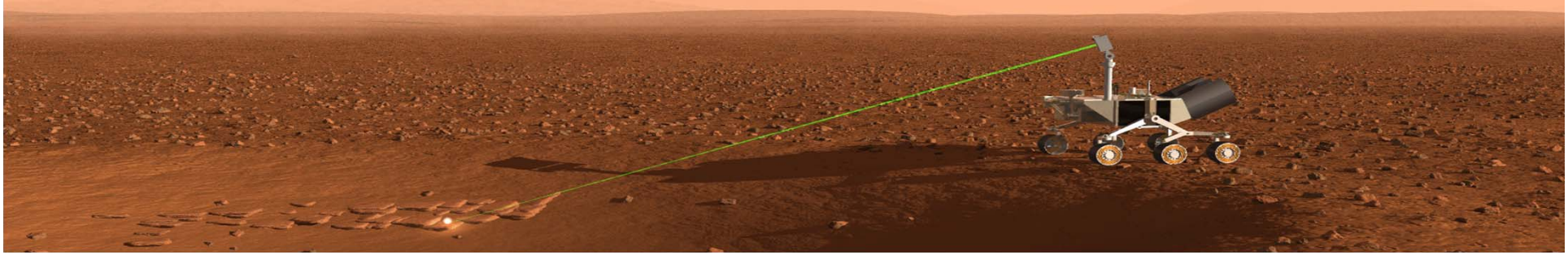
Chemical Matrix Effects Complicate Quantitative Analysis



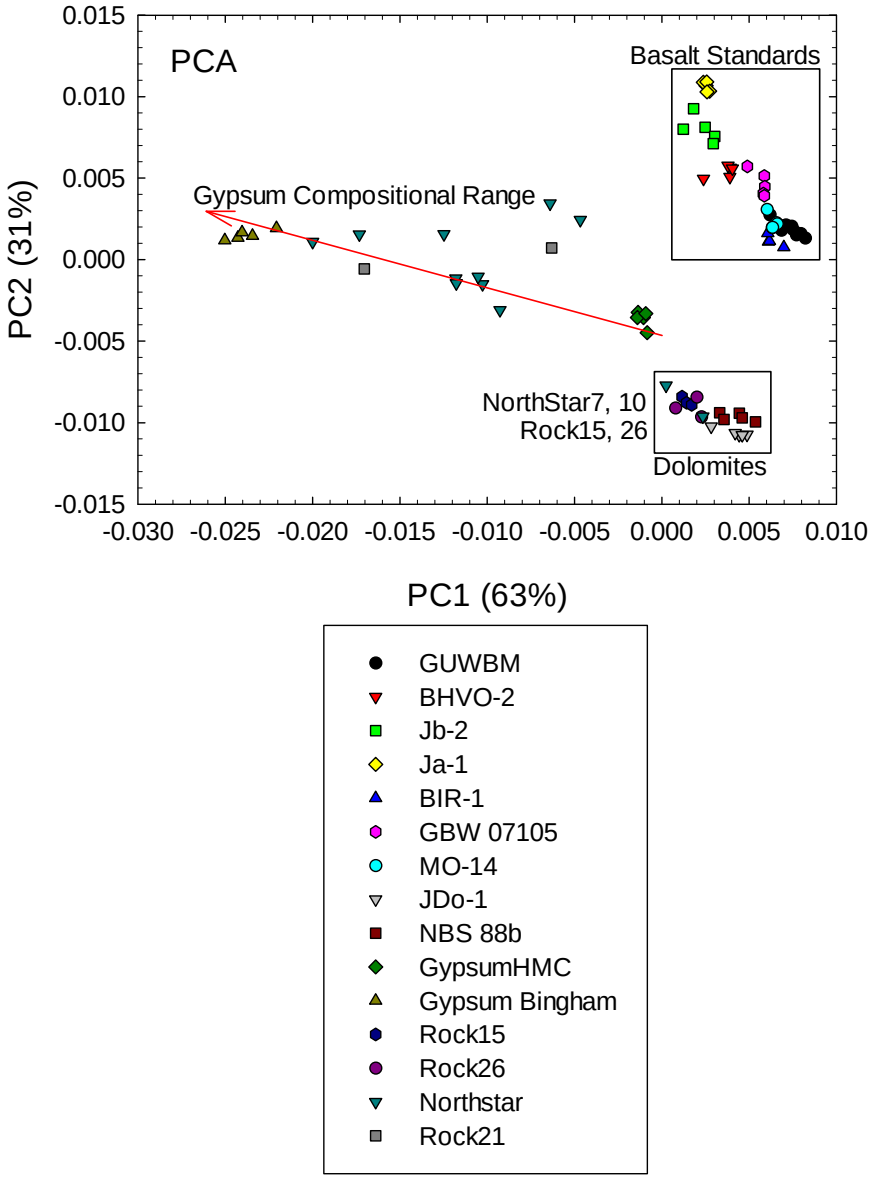
- Conventional Elemental Analysis
  - Peak Area or Height vs. Concentration
  - Each Peak is Analyzed Independently
- Sample Elemental and Molecular Composition Influences:
  - Laser-to-Sample Coupling Efficiency
  - Chemical Reactions within the Plasma
  - Collisional Quenching
- Chemical Matrix Effects
  - Increase Scatter and Uncertainty
- Chemical Matrix Effects Compensation
  - Cal-Free LIBS
  - Various Normalization

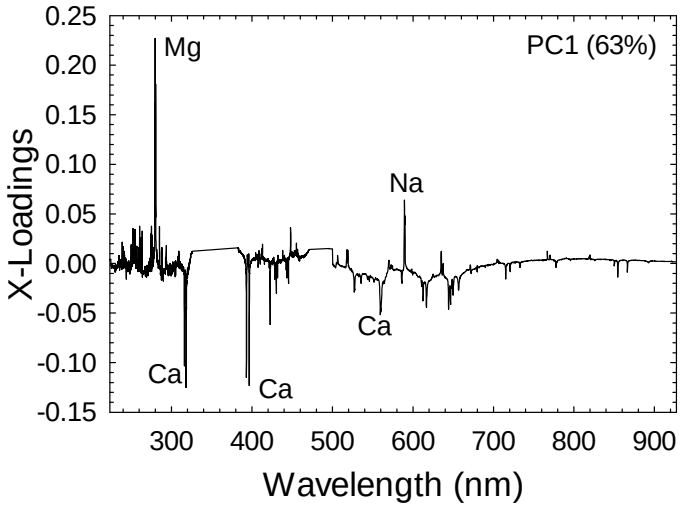
Conclusions

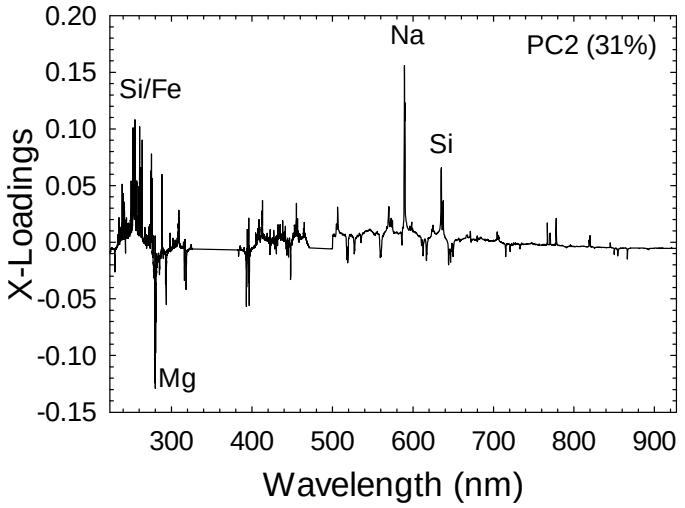
- Laser Induced Breakdown Spectroscopy
  - Multivariate Analysis
    - Partial Least Squares (PLS)
      - Quantitative Elemental Analysis
    - Principal Components Analysis (PCA), Independent Components Analysis (ICA)
      - Speciation
- Integrated Raman – LIBS Spectroscopy
  - Direct measure of both Elemental and Molecular Structure.
  - Rapid Quantitative Elemental & Mineralogical Analysis
  - No External Arm is Required
  - No Sample Preparation Required
  - Avoids Risks Associated with Sample Collection and Transfer into Rover/Lander
- LIBS Spectra are More Complicated Under Venus Conditions
  - Than on Earth or Mars
  - Pressure Broadening is Observed
  - Optimal Spectral Resolution needs to be Determined
  - Turbulence Don’t Seem to be a Problem



Principal Components Analysis (PCA)







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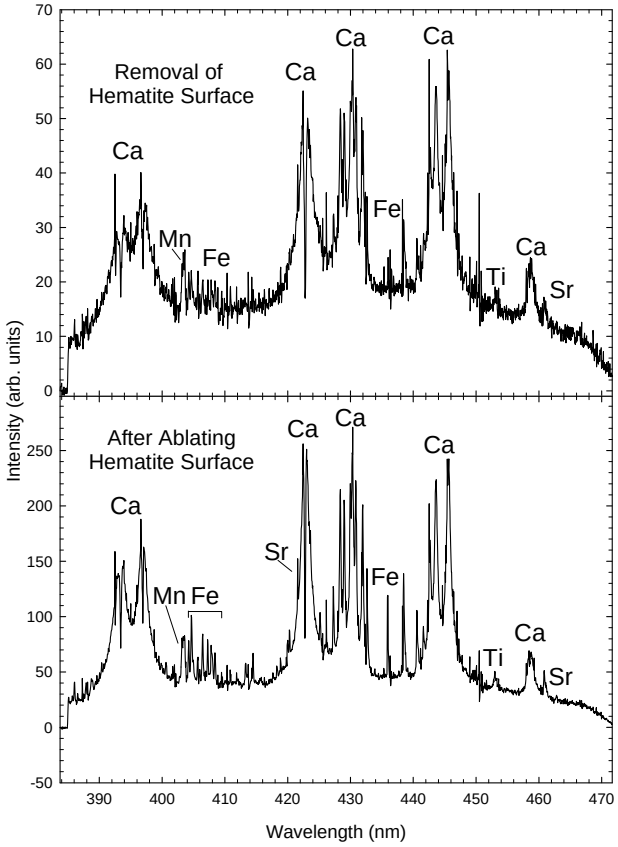
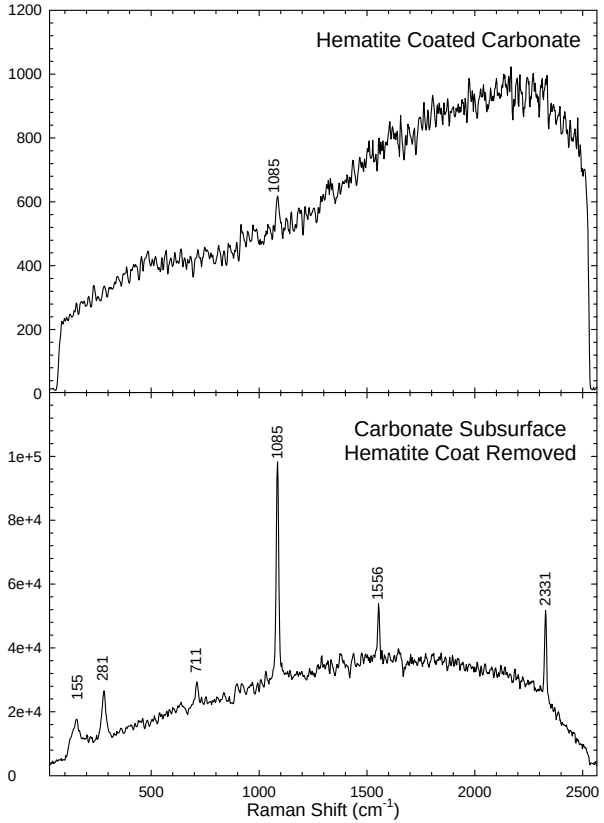
Hematite coated Calcite





Ablate Hematite Coating with LIBS laser

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Raman – LIBS Integrated Solution

- Laser
  - 1064nm and 532nm
- Chromatic Aberration
  - Beam Expander
- Different Focal Lengths
  - LIBS with Focused 1064nm
  - Raman with Unfocused 532nm
- Simultaneous Raman – LIBS Spectra

Calcite ($CaCO_3$)