Miniaturized LIBS-Raman Spectrometer for in-situ Exploration

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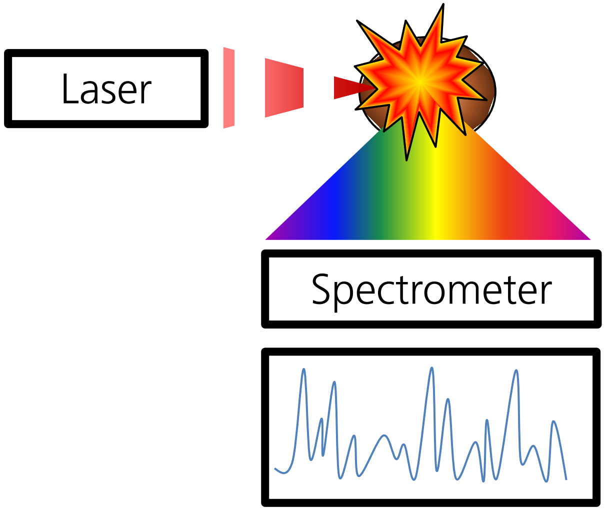
LIBS and Raman Spectroscopy

Science goal → geochemistry, mineralogy

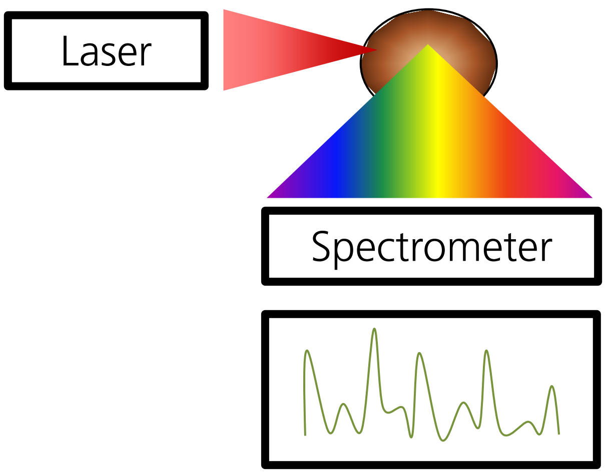


LIBS (Laser-Induced Breakdown Spectroscopy)

radiation from a high-power pulsed laser is focused onto a sample

→ ablation of material, plasma production

atomic transitions → **Elemental composition**



Raman Spectroscopy

nondestructive method

monochromatic light (laser) is inelastically scattered → energy of exciting photons is shifted. shift characteristic for the material

→**Molecular structure, identification of minerals**

Advantages for in-situ exploration:

combined: <u>complementary information</u>

high sensitivity mineralogical characterization

no sample preparation, high spatial resolution, simultaneous multi-element detection, fast analysis (secs to mins), removal of dust layers, **depths profiling**,…

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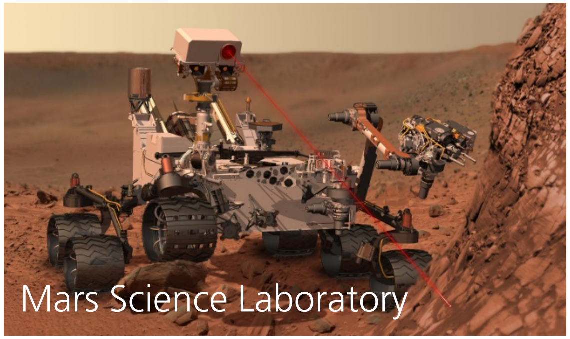
LIBS and Raman for Solar System Exploration



ChemCam (LIBS) on NASA's MSL

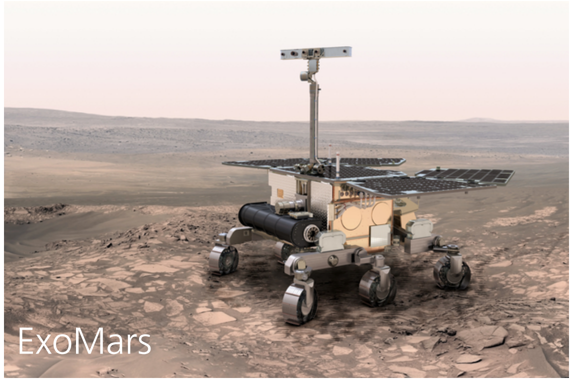
Remote (up to 7m), instrument <10 kg (telescope)

(Maurice et al., 2012; Wiens et al., 2012)

→ SuperCam on NASA's Mars 2020 mission

Remote **LIBS & Raman** *(Clegg et al., 2015; Maurice et al., 2015)*

UV-Raman SHERLOC *(Beegle et al., 2015)*



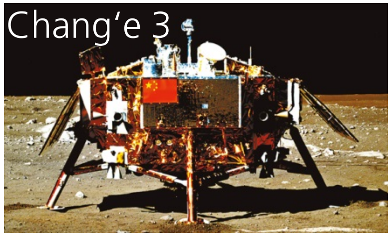
Raman on ESA's Exomars Rover 2020

On-board Raman, crushed samples analyzed inside, 2.3 kg

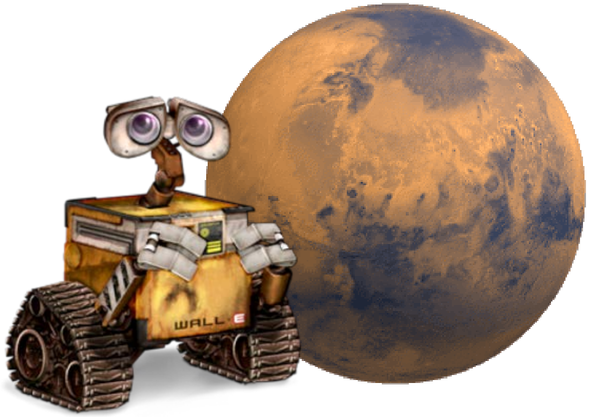
(e.g., Rull et al., 2014)

Payload under discussion for several mission proposals:

- ESA: Phobos lander (M5 call)
- Russia: Luna Resurs Program
- Japan: Phobos lander
- China: Chang'e moon lander



Research Topics



Robotic exploration

Mars (p = 7mbar, CO_2 atmosphere)

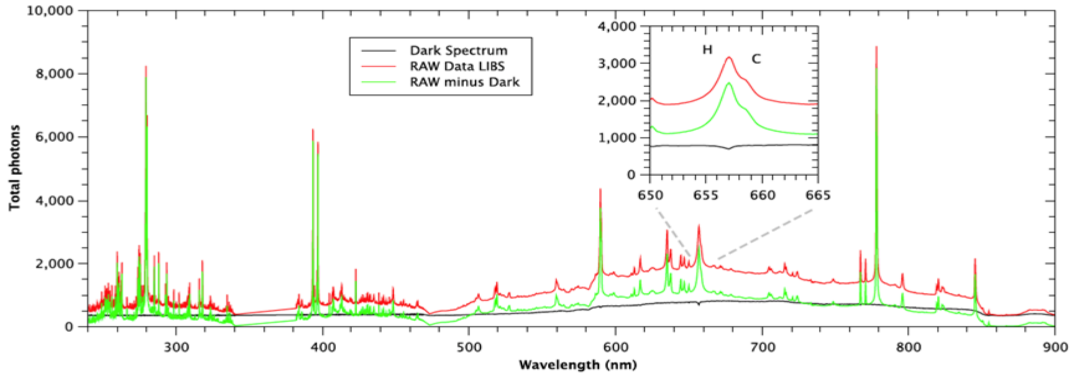
- salts (sulfate, chlorides, perchlorates,…)
- <u>Frozen salt-solutions (ices)</u>

- Meteorites
- Organic materials → Talk by M. Baqué

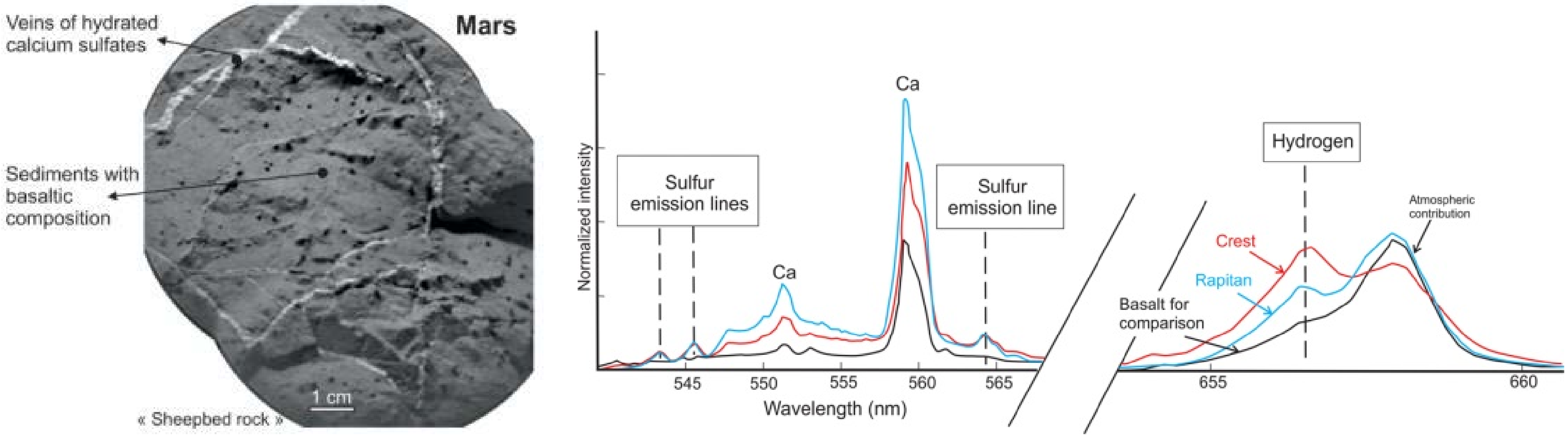
Low pressure environments

LIBS Spectroscopy - Science

- elemental analysis
- simple, fast, direct
- sensitive to all elements, incl. H
- no sample preparation (self-cleaning, penetrating up to mm)
- standoff remote analysis (up to a few meters)



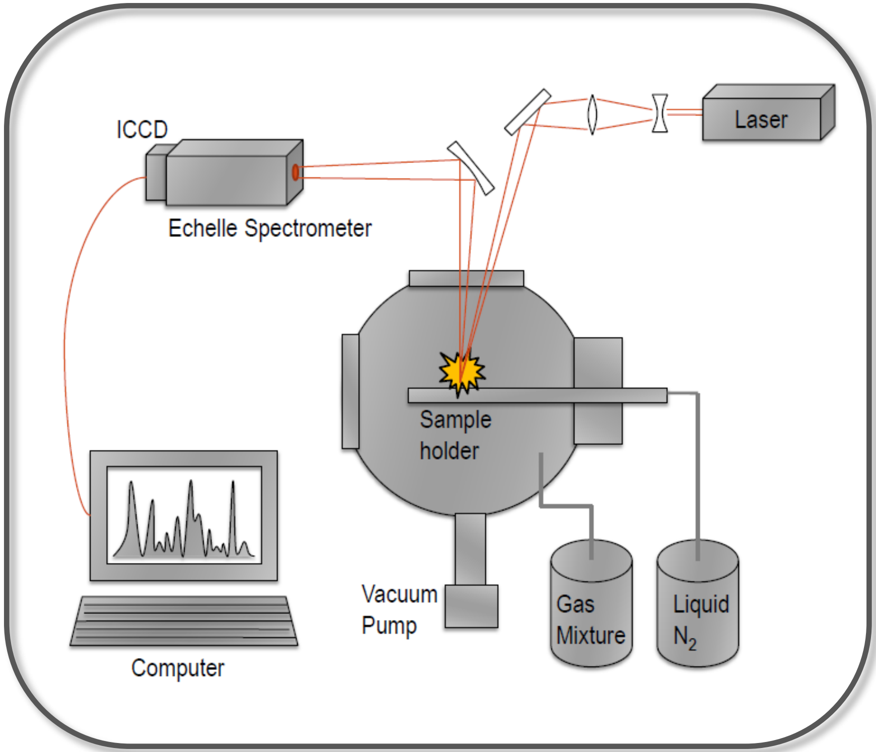
H in first martian ChemCam LIBS spectrum (Schröder et al., 2015)



Hydrated Ca-Sulfates (Nachon et al., 2014)

LIBS Laboratory Set-up DLR

- Simulation of planetary atmospheres:
- **Martian analogue gas mixture (95.55 %vol. CO_2, 2.7 %vol. N_2, 1.6 %vol. Ar, and 0.15 %vol. O_2)**
- Pressure range $1 \cdot 10^{-1}$ to $1 \cdot 10^{3}$ mbar
- Temperature range 140 - 300 K, ±0.5 K
- Probe on xyz-stage for alignment
- Video surveillance



LIBS Laboratory Set-up DLR

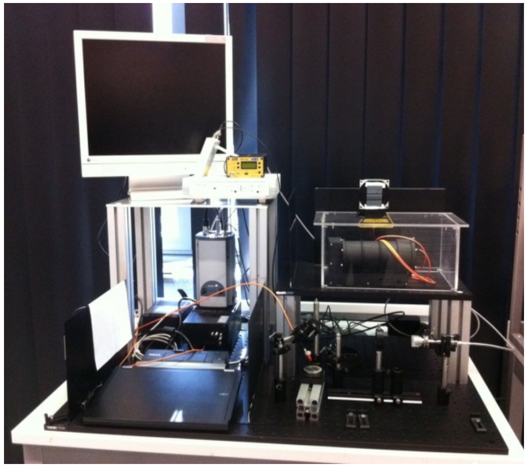
Exciting Laser:

(1) Continuum Model Inlite
- Nd:YAG @ 1064 nm
- energy: up to 250 mJ

(2) Neolase
- Nd:YLF @ 1053 nm
- energy: 0.1 – 5 mJ

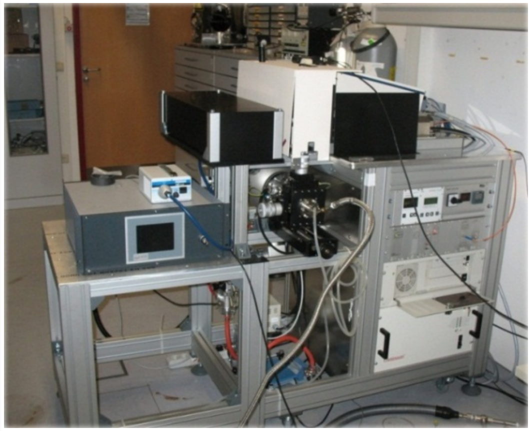
(3) Prototype laser
- Nd:YLF @ 1053 nm
- energy: up to 1.8 mJ

Mini-LIBS set-up

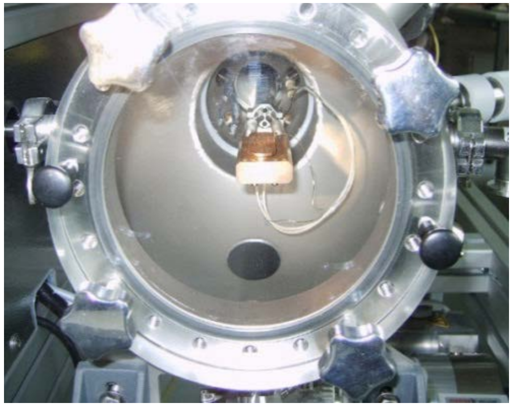


Mini-LIBS laser

Laboratory set-up with two lasers



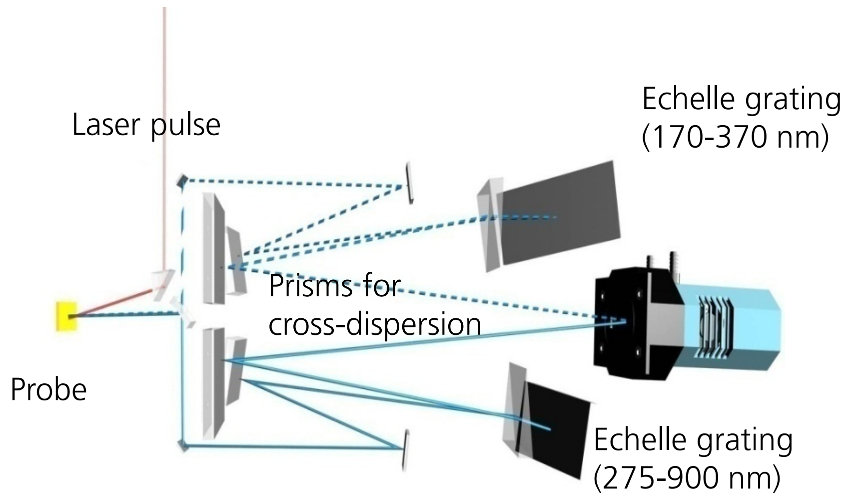
Planetary simulation chamber

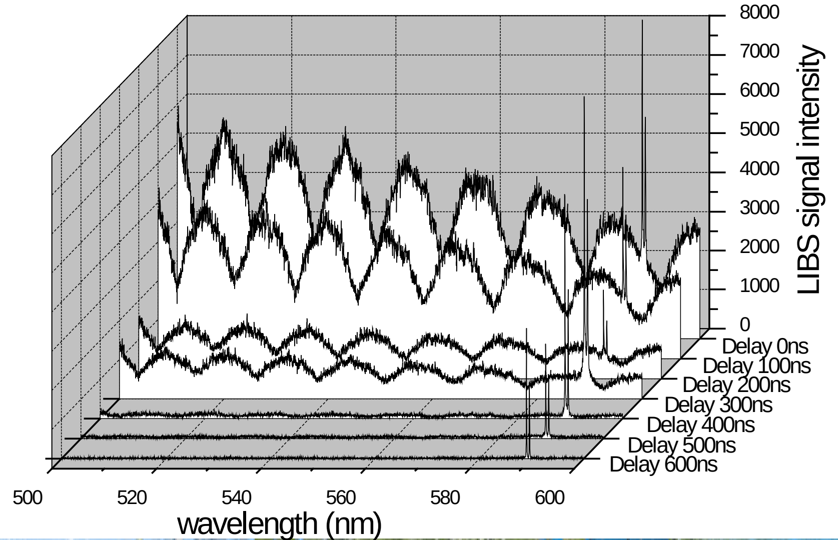


LIBS Laboratory Set-up DLR

Spectrograph (Aryelle Butterfly LTB)

- wavelength coverage: 191-390 nm (UV), 280-900 nm (Vis/NIR)
- spectral resolution: 14-96 pm ($\lambda/\Delta\lambda$=14000/9400)
- wavelength calibration with a Hg spectral lamp
- detector: ICCD (Andor)





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LIBS: Salts and frozen salt solutions

HRSC. crater near North Pole with water ice (ESA, DLR, FU Berlin, G. Neukum)

Ice & salts on Mars

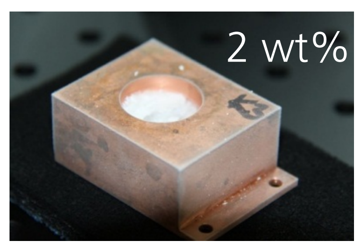
- Chlorides and sulfates
- Hydrated salts
- Essential for Mars surface geochemistry
- Brines
- Astrobiology

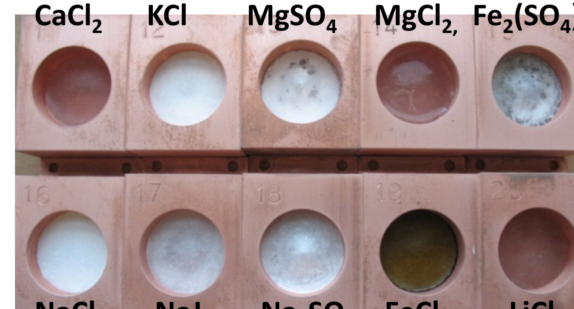
Phoenix landing site

Investigated salts:

$CaCl_2$, $CaSO_4$, KCl, K_2SO_4, $MgCl_2$, $MgSO_4$,
NaCl, Na_2SO_4, $Fe_2(SO_4)_3$, $FeCl_3$
Perchlorates: $Mg(ClO_4)_2$, $NaClO_4$

Different eutectic behaviours and appearances (solidity, opacity, colour variations,…)





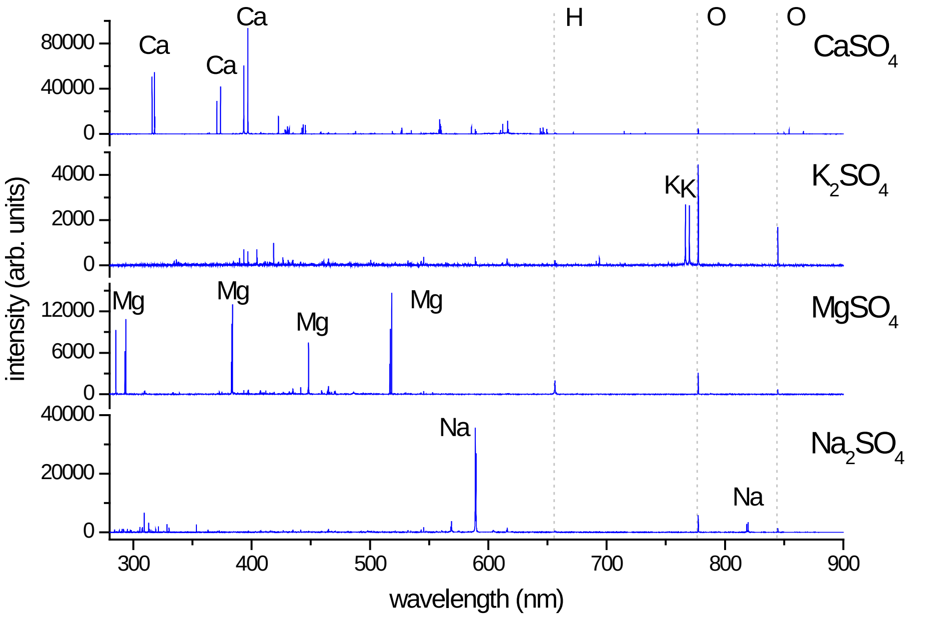
LIBS: Salts and frozen salt solutions

LIBS spectra

- Alkali & earth alkaline elements easy to identify
- Halogens such as Cl, S only weak emission

Multivariate Data Analysis (MVA) allows for discrimination

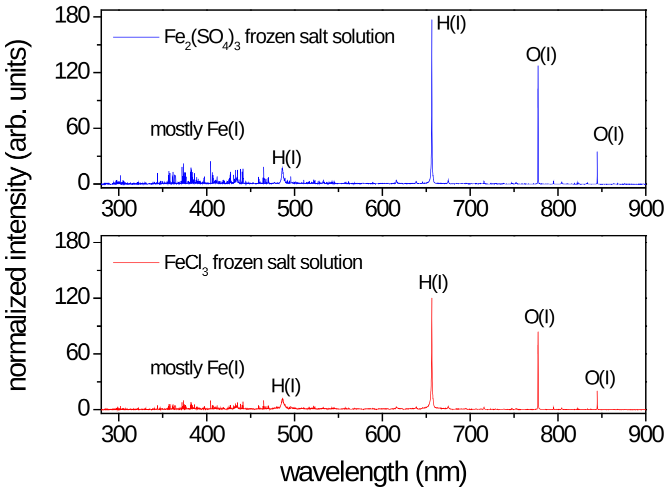
- Principal component analysis (PCA)
- Soft independent modeling of class analogy (SIMCA)
- Partial least-squares discriminant analysis (PLS-DA)



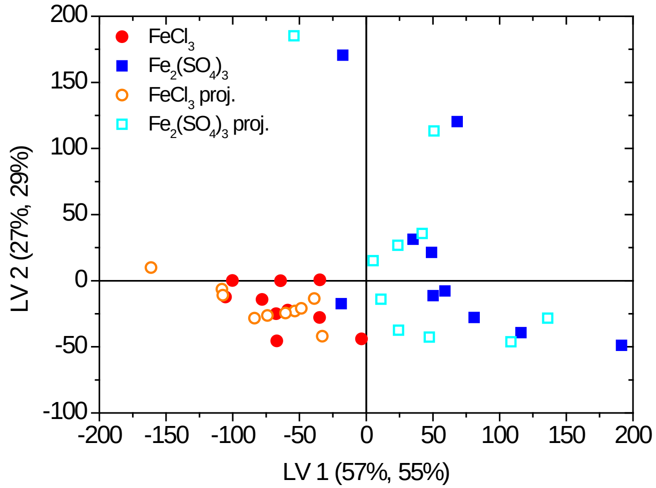
S. Schröder et al., 2013

LIBS: Salts and frozen salt solutions

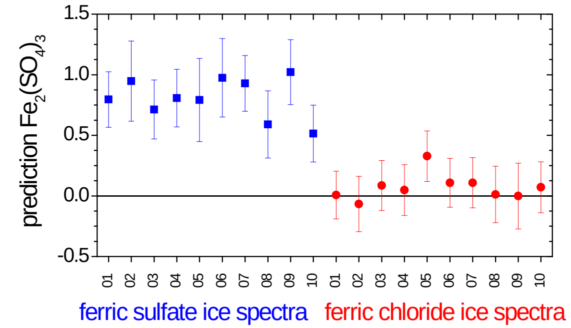
Ferric salts in frozen salt solution - $Fe_2(SO_4)_3$ vs. $FeCl_3$



PLS model



classification



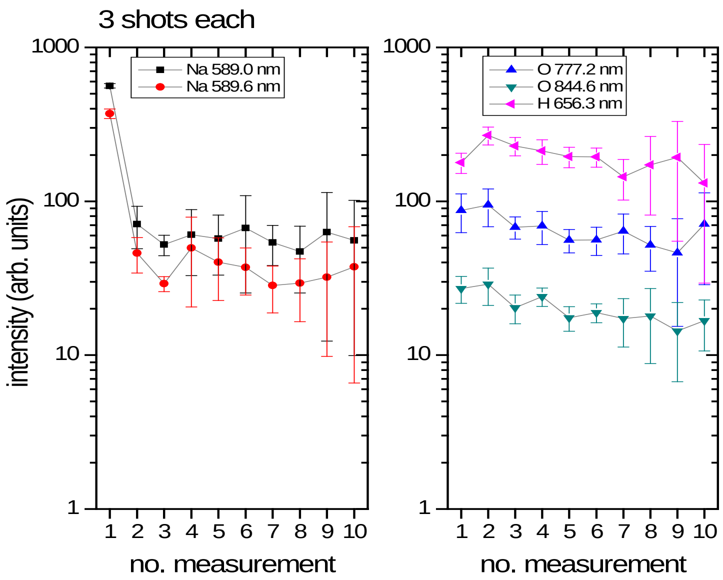
S. Schröder et al., 2011

LIBS: Salts and frozen salt solutions

Depth profiling (up to mm in soft matrix)

- Salt layer forms on the samples surface
- Emission line intensities of Na and Cl rapidly decrease
- O and H remain almost constant (but error increases due to plasma confinement)

→**Subsurface can be probed**
→**Dust layers can be removed**
→**Weathering layers can be investigated**

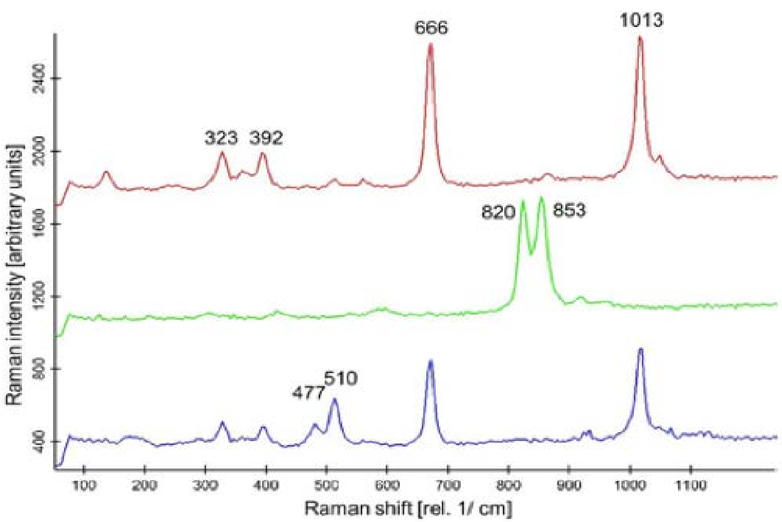


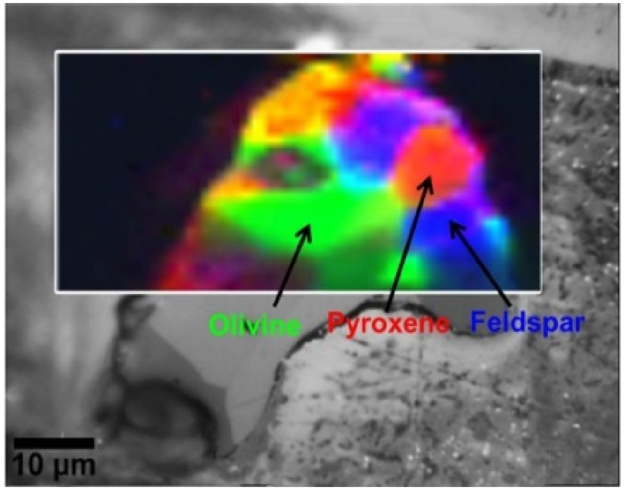
LIBS data from NaCl-frozen salt solution

S. Schröder et al., 2012

Raman Spectroscopy - Science

- structural and chemical information about the system (molecules, crystals,..)
- complementary to IR and to LIBS (elemental composition)
- investigation of minerals, brines and biological samples and mixtures
- AND terrestrial contamination (e.g. propellant)
- fast – full data acquisition in less than minutes
- non destructive





Raman spectra Hayabusa particles (Böttger et al., 2014)

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Raman: Vostok lake ice with inclusions

Collaboration with S. Bulat (FSBI Petersburg)

Objective:

Study inclusions (~mm) in ice with confocal Raman microscope

Special challenge: do not melt the ice with the laser!

Results:

Inclusion in original ice (never molten) contains anatase (TiO_2) and <u>amorphous carbon</u>

2014 – 5G-3 3607m accretion I ice sample

Sample cryo-holder with Vostok lake ice with inclusion

Böttger et al., submitted

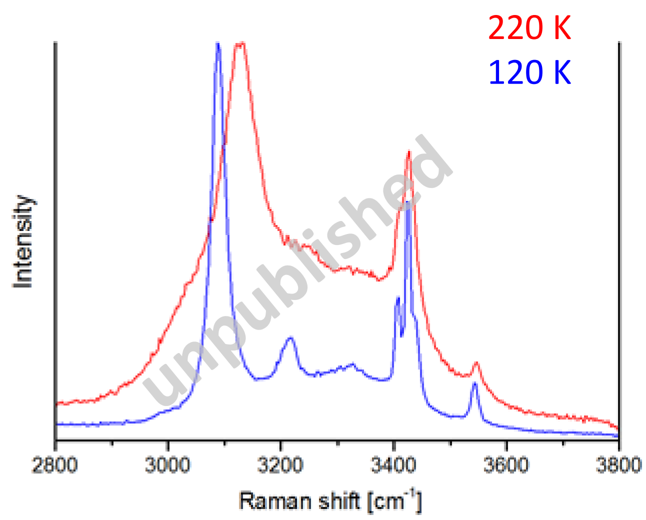
Raman: Salts and frozen salt solutions

Samples: binary system of H_2O and different salts

- diatomic salts: NaCl, KCl, LiCl, NaI, NaBr
- polyatomic salts (non-sulfates): $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$
- polyatomic salts (sulfates): Na_2SO_4, K_2SO_4, $CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot H_2O$, $MgSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3 \cdot xH_2O$

Results:

- most of the frozen salt solutions could be identified using Raman spectroscopy
- The combination of Raman spectroscopy, PCA and cluster analysis is an appropriate method for the detection, differentiation and identification of these frozen salt solutions



Hanke et al., in preparation

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Summary: Salts and frozen salt solutions

- Multivariate data analysis methods **are suitable** for LIBS and Raman analysis of frozen salt solutions
- **Spectra of various salts pure, in soil, and as frozen salt solutions can be identified**
- **Inclusions can be identified**
- Improvement can be obtained by:
  - averaging multiple spectra
  - preprocessing of the data (i.e. background subtraction)
  - analysis chains & local application of MVA
  - depends on samples

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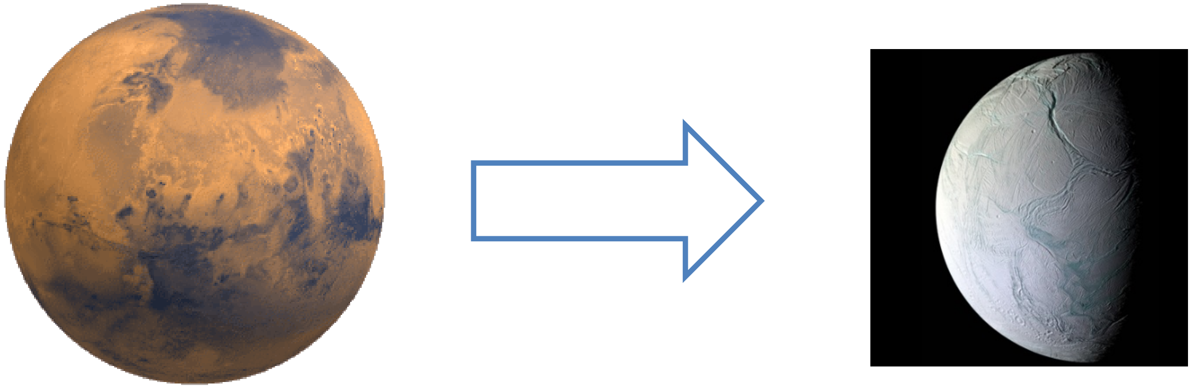
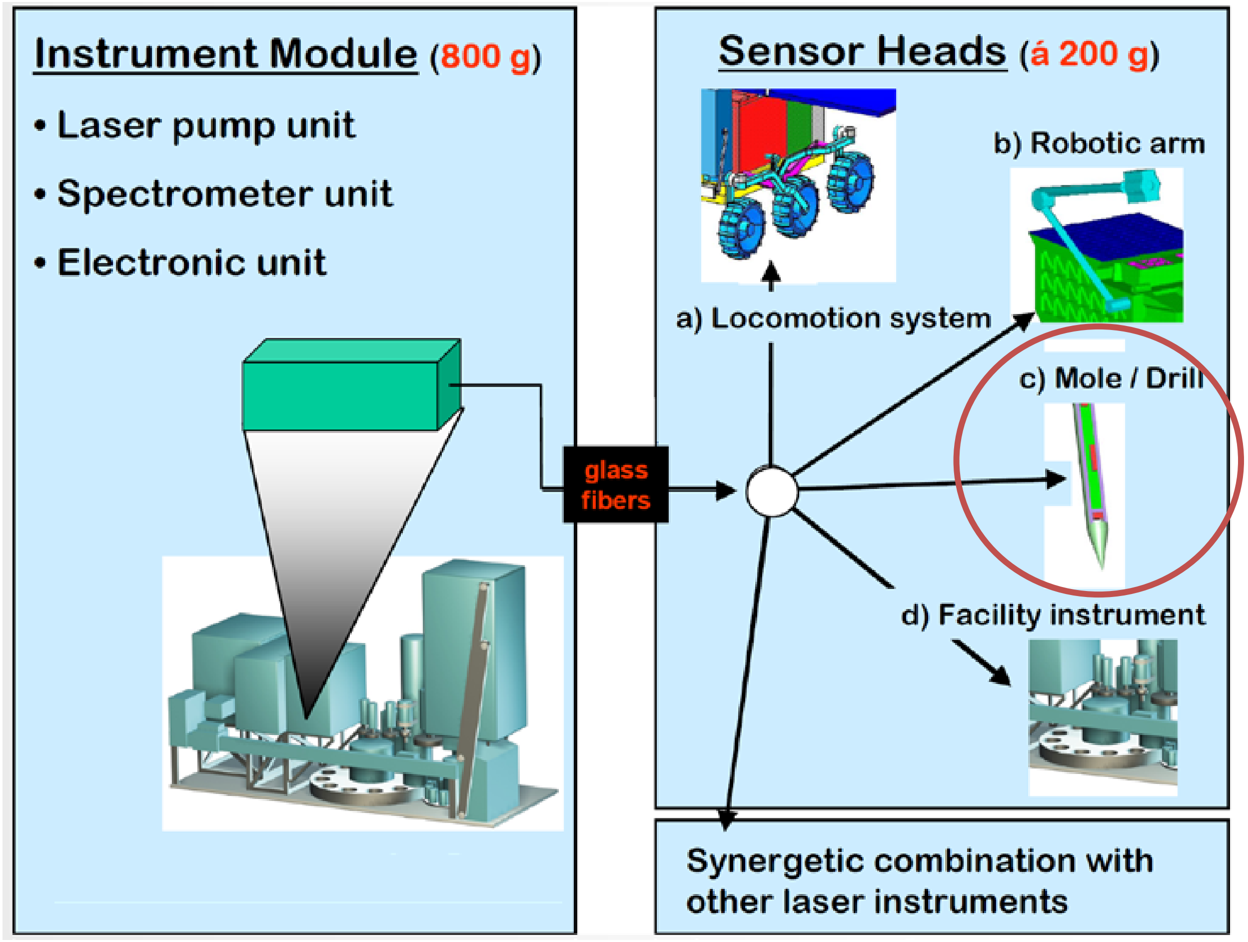


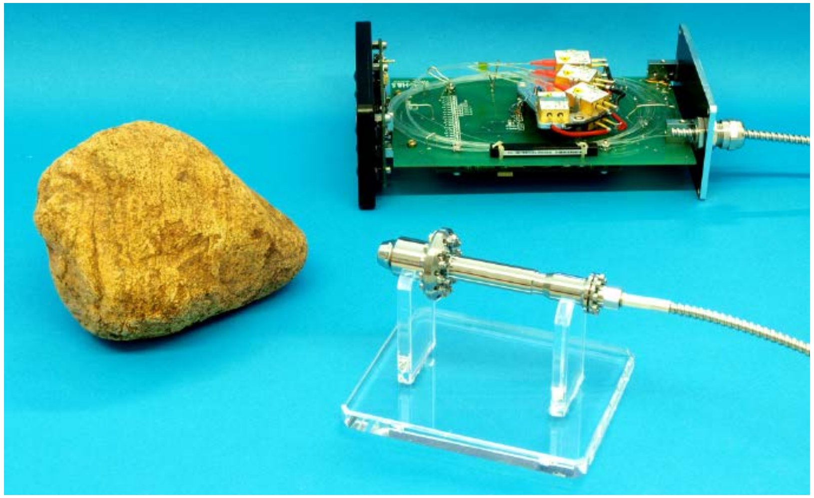
Robotic Mini-LIBS/Raman Spectrometer



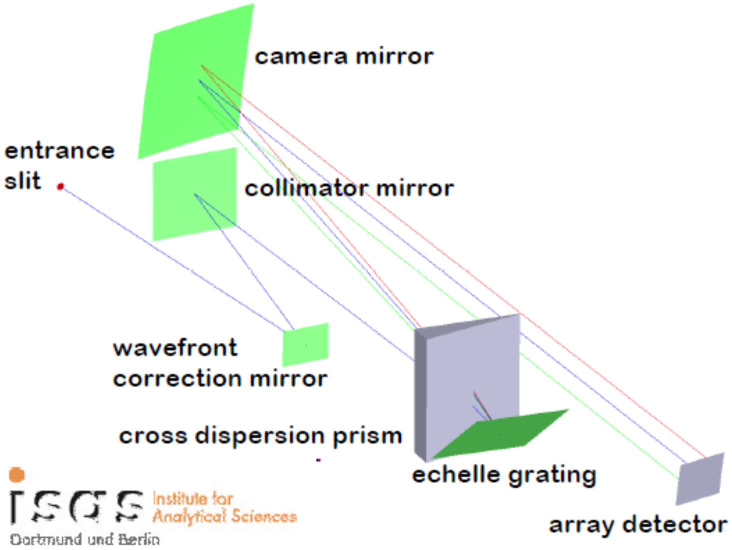
Robotic Mini-LIBS/Raman Spectrometer

Integration of lasers into compact Sensorhead
cooperation with FBH, Berlin (Raman-Laser)
cooperation with LZH, LTB, vH&S: LIBS

Mass of laser head ~ 25g
Total mass ~ 216g



Mini-Echelle Spektrometer



Developed by ISAS

- Dimensions 16 x 7 x 6 cm
- Range: 240 - 780 nm
- Resolution 0.05-0.1 nm
- Accuracy: 5 – 20 pm
- Image Area: 8 mm x 8 mm

→ Total Instrument ~ 3 kg

Summary

- LIBS and Raman spectroscopy very suitable for solar system exploration
- Complementary information: elemental analysis and molecular structure
- Depth profiling up to mm
- Suitable for identification of salts, salt-ice matrices, and inclusions
- can be integrated into one compact instrument ~3 kg
- Sensorhead could be attached to mole or drill