In Situ Composition Analysis of Planetary Surfaces by Laser-Based Mass Spectrometry

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Introduction

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- Science Scope
  - Elemental composition of solids (soil, rock, ice)
  - Derive the chemical composition and infer mineralogical composition
  - Isotopic composition
  - Bio markers, bio molecules
  - Trace elements
  - Toxic substances
  - Context science
- Missions
  - Russian mission Phobos-Grunt to the Mars moon Phobos
  - Exploration of the Jupiter system
  - European mission to planet Mercury, BepiColombo

Why Laser Ablation?

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- Traditional solid sample ionization:
  - E.g. dissolution and inductively coupled plasma, glow-discharge, spark source, particle bombardment
  - All require sample preparation and controlled gas pressure
- Laser ablation/ionisation couples well with TOF-MS
  - Low mass, size and power requirements
  - Direct interface to mass analyzer
  - Appropriate duty cycle
- Depth profiling possible
- Laser ablation/ionisation TOF-MS have been previously built for space:
  - LIMA-D on Phobos mission
  - LASMA on Phobos-Grunt
  - LAMS from APL, John Hopkins University
    - Still at prototype stage
    - Based on earlier IKI design
  - LMS for BepiColombo/MSE

Focusing of Ablation Laser

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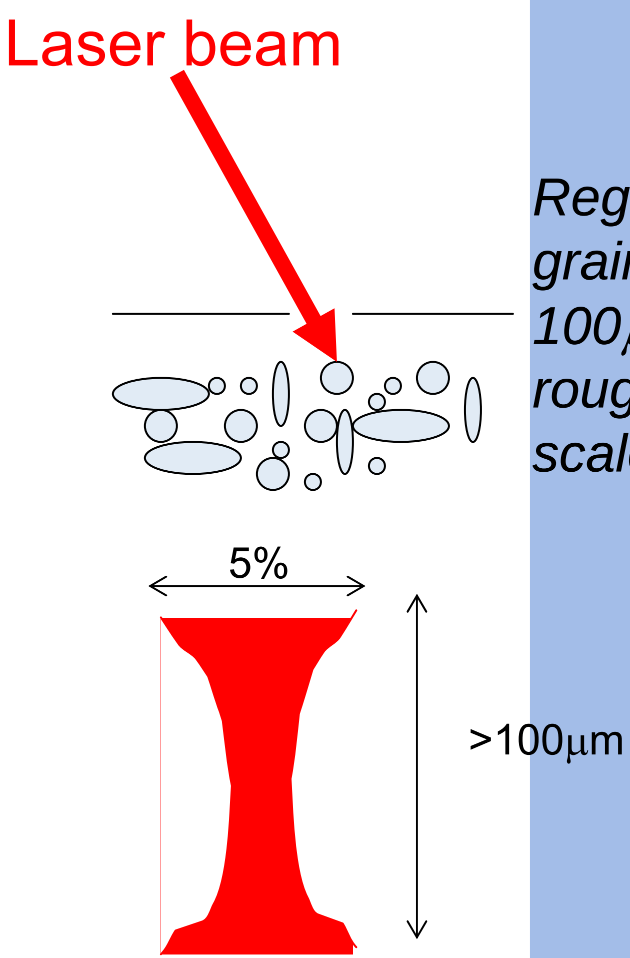

Regolith target, grain size 10–100μm, therefore rough on this scale.

- Depth of focus must be at least 100 μm (±10% irradiance points)
- Irradiance should ideally be constant across the focus
- Require (1–4)·10^9 W/cm^2 at

Too little power (<10^8 W/cm^2): severe elemental fractionation due to thermal effects, low yield, polyatomic interferences

Too much power (>10^{10} W/cm^2): increased ion energy dispersion, high energy tail on peak shape, multiply charged ion interferences

Possible Laser Implementation

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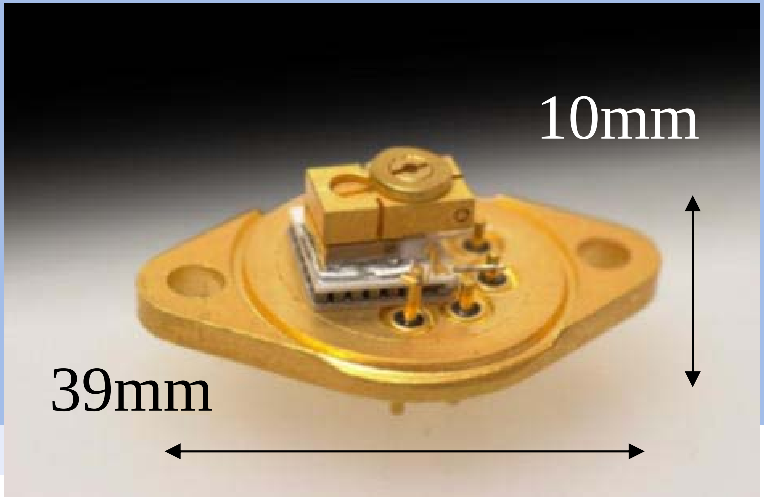
- Passively Q-switched diode pumped microchip laser (Nd:YAG=1064nm)
  - typically 10 μJ,1 ns pulse for 10 kW peak power at 10 kHz repetition rate
  - when focused to 20 μm spot gives about 5 GW/cm^2
  - ⇒ 0.1 μm depth/pulse or 10^4 ions
- Beam delivery
  - Need high intensity
  - Short focal length lens
  - Must avoid deposits on lens
  - Hollow optical fibre?
- Requires 1.85V, 1.4A (2.6W)



Prototype of Laser Mass Spectrometer (LMS) for the Mercury Lander

U. Rohner, J. Whitby, and P. Wurz, Meas. Sci. Technol., 14 (2003), 2159–2164.

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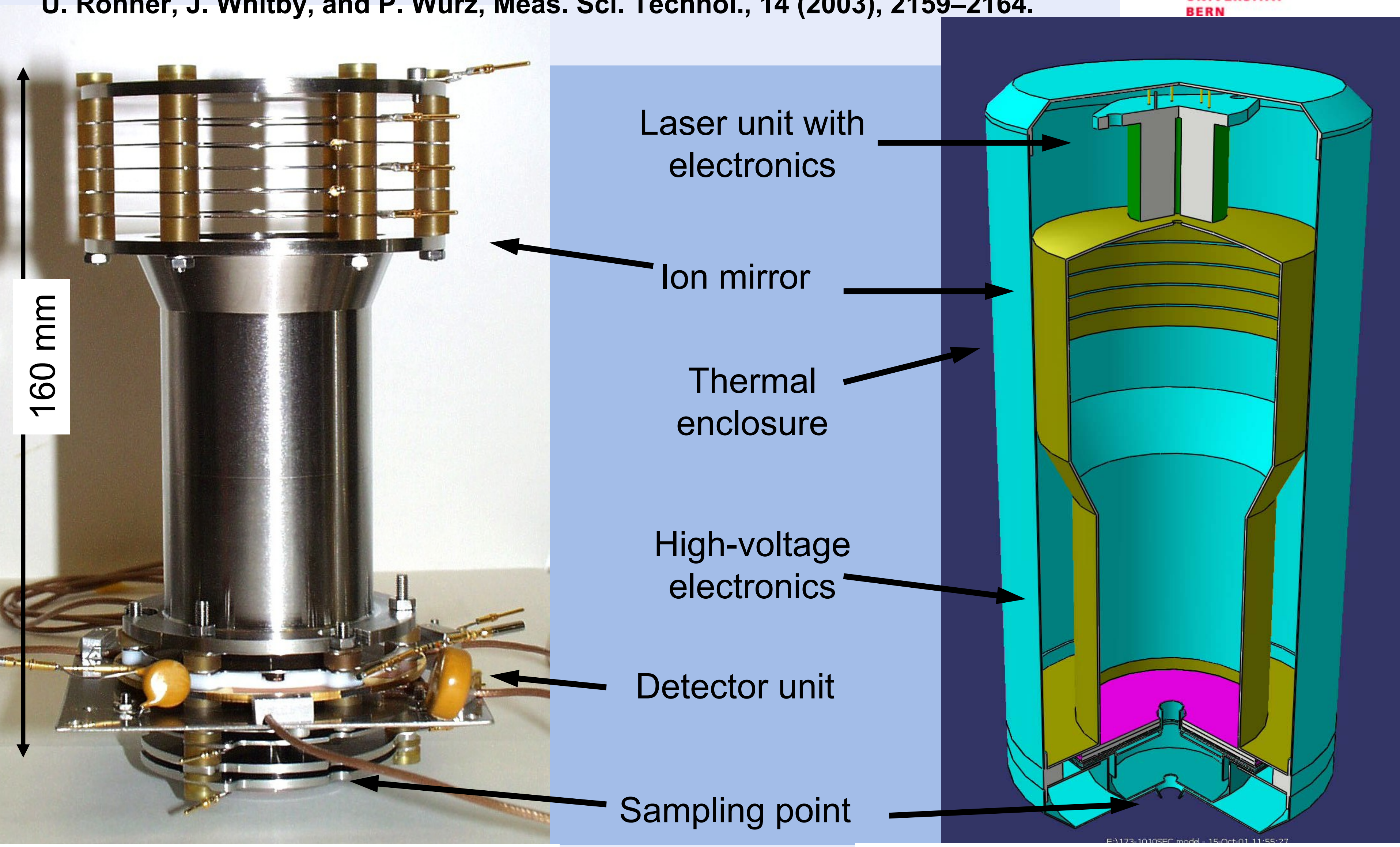
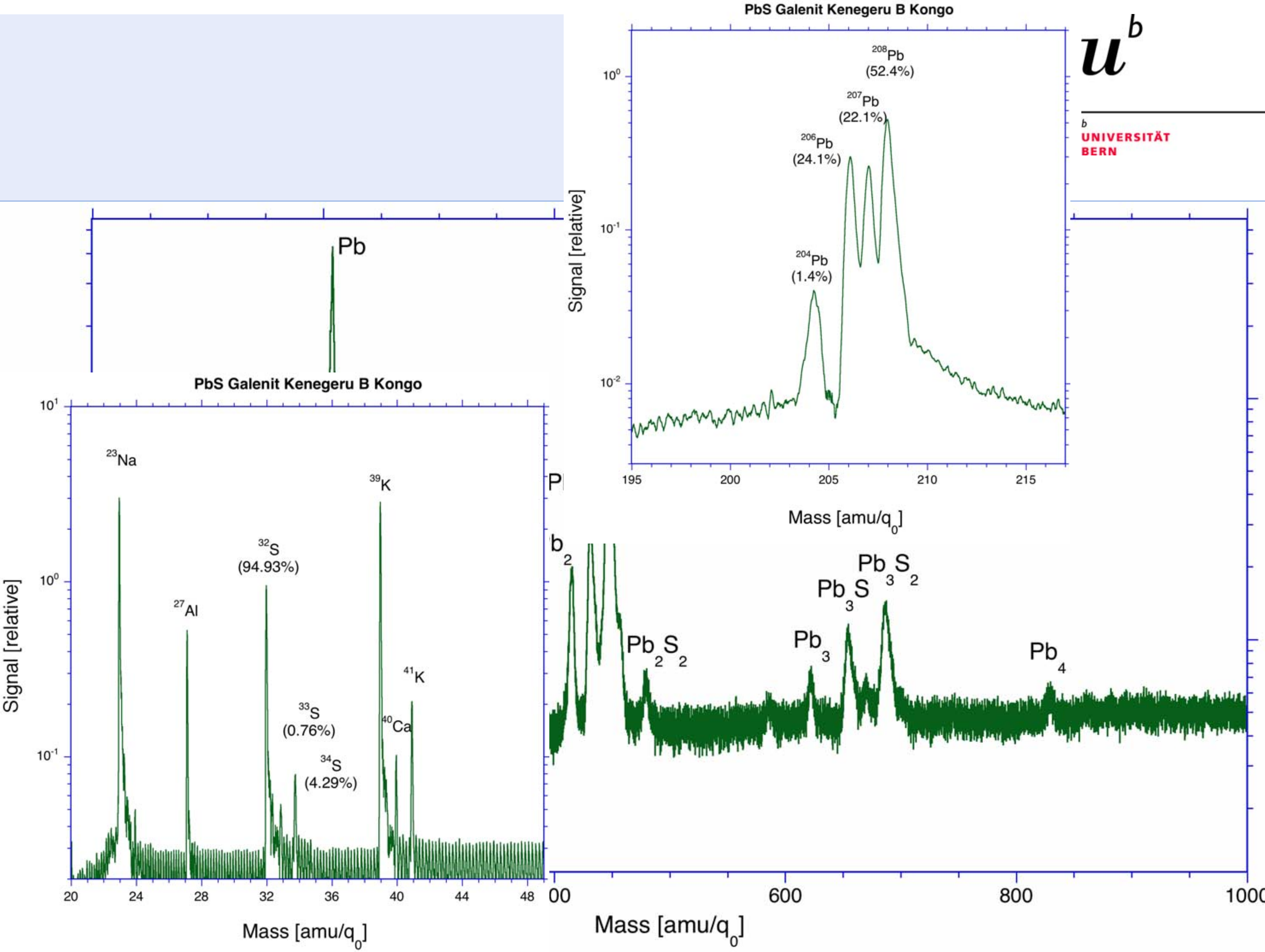


Prototype

Flight Design


PbS Galenit Kenegeru B Kongo
Signal [relative]
Mass [amu/q0]
208Pb (52.4%)
207Pb (22.1%)
206Pb (24.1%)
204Pb (1.4%)
10^0
10^-1
10^-2
195
200
205
210
215
PbS Galenit Kenegeru B Kongo
Signal [relative]
Mass [amu/q0]
23Na
27Al
32S (94.93%)
33S (0.76%)
34S (4.29%)
39K
40Ca
41K
10^1
10^0
10^-1
20
24
28
32
36
40
44
48
Pb
Pb2S2
Pb3
Pb3S
Pb3S2
Pb4
600
800
1000
Mass [amu/q0]

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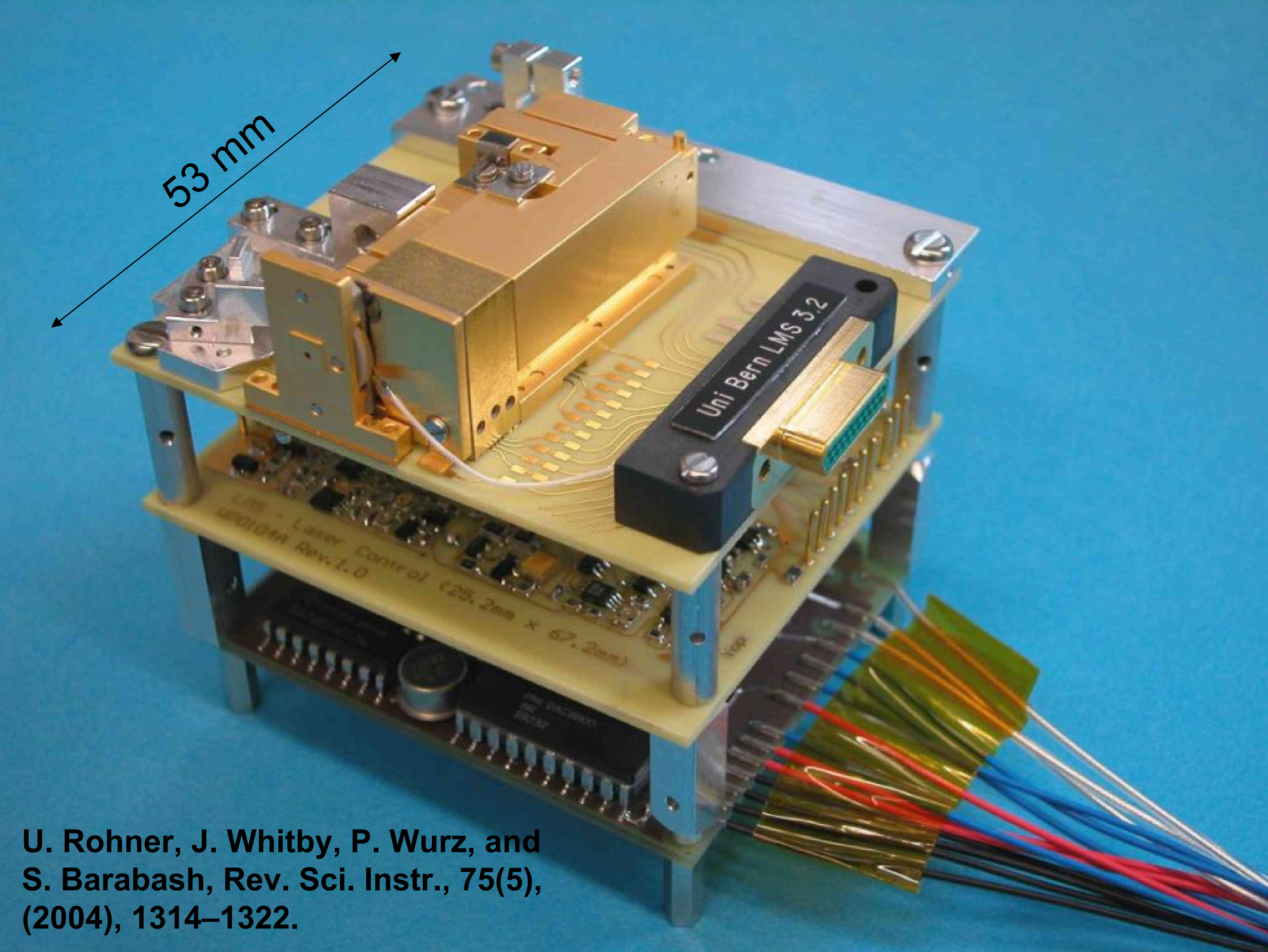
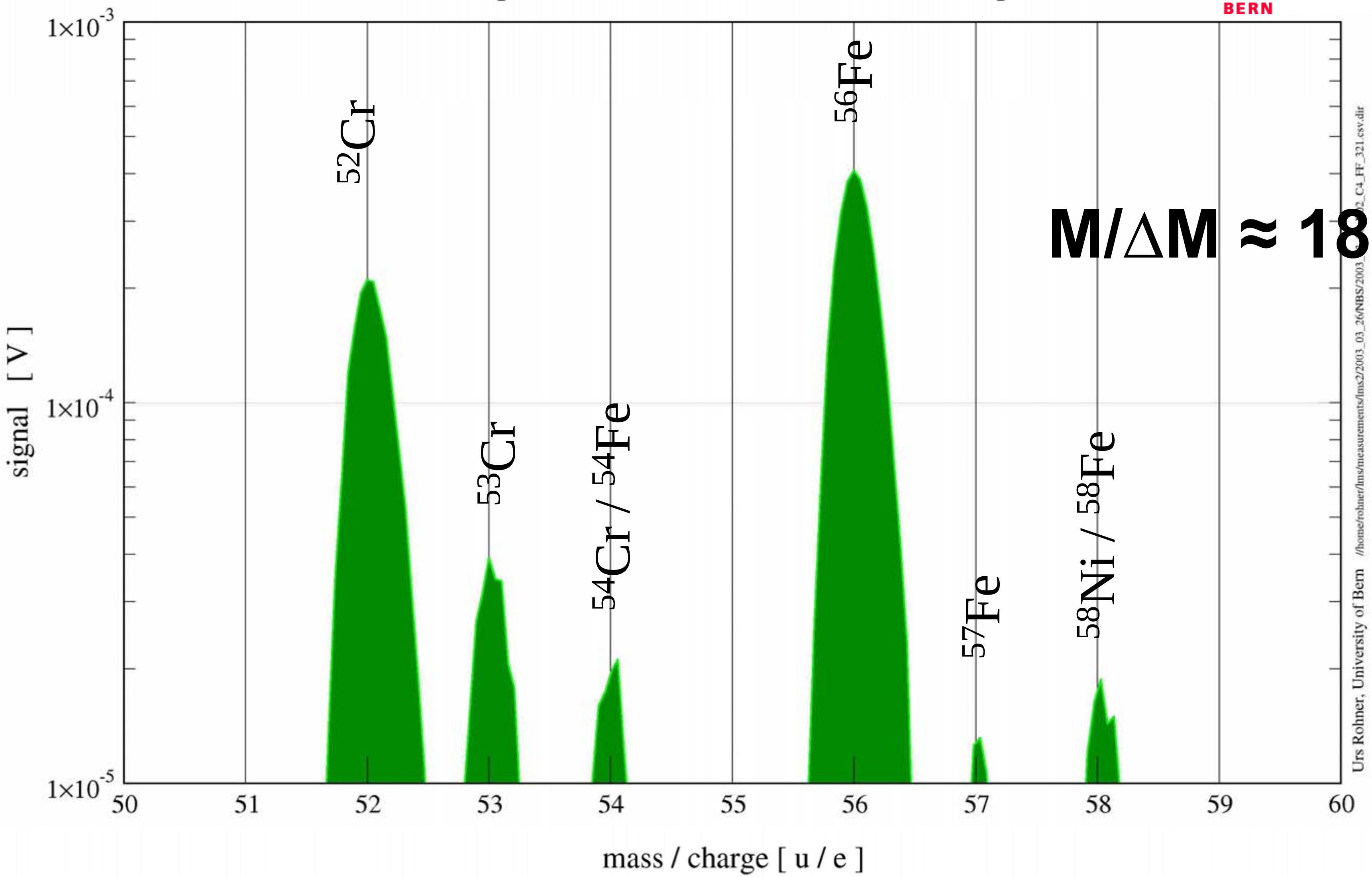


U. Rohner, J. Whitby, P. Wurz, and S. Barabash, Rev. Sci. Instr., 75(5), (2004), 1314–1322.

IR-Laser Mass Spectrum

Lander Mass Spectrometer LMS2 (Roverversion for Bepi Colombo)



M/ΔM ≈ 180

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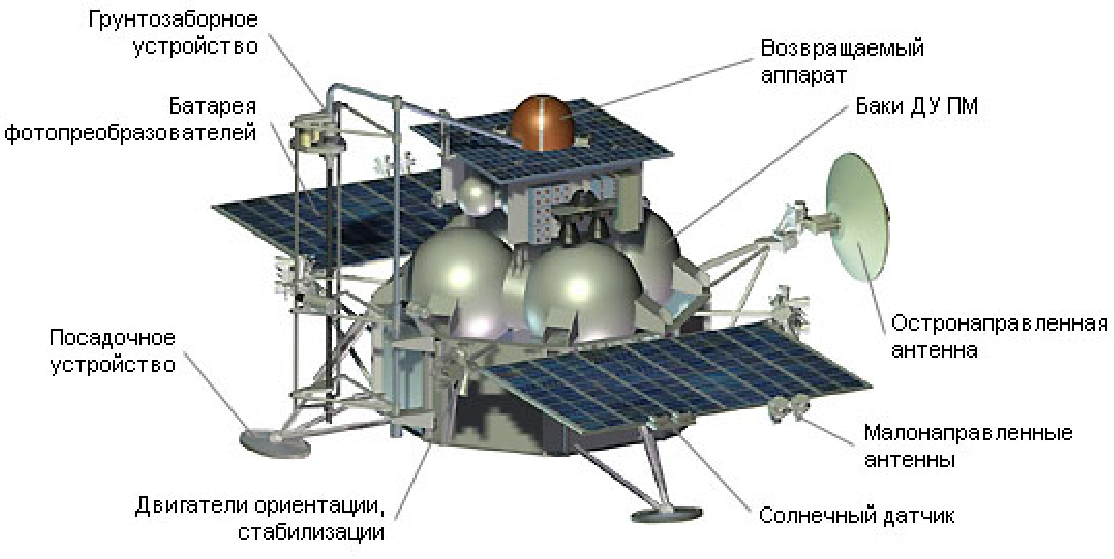
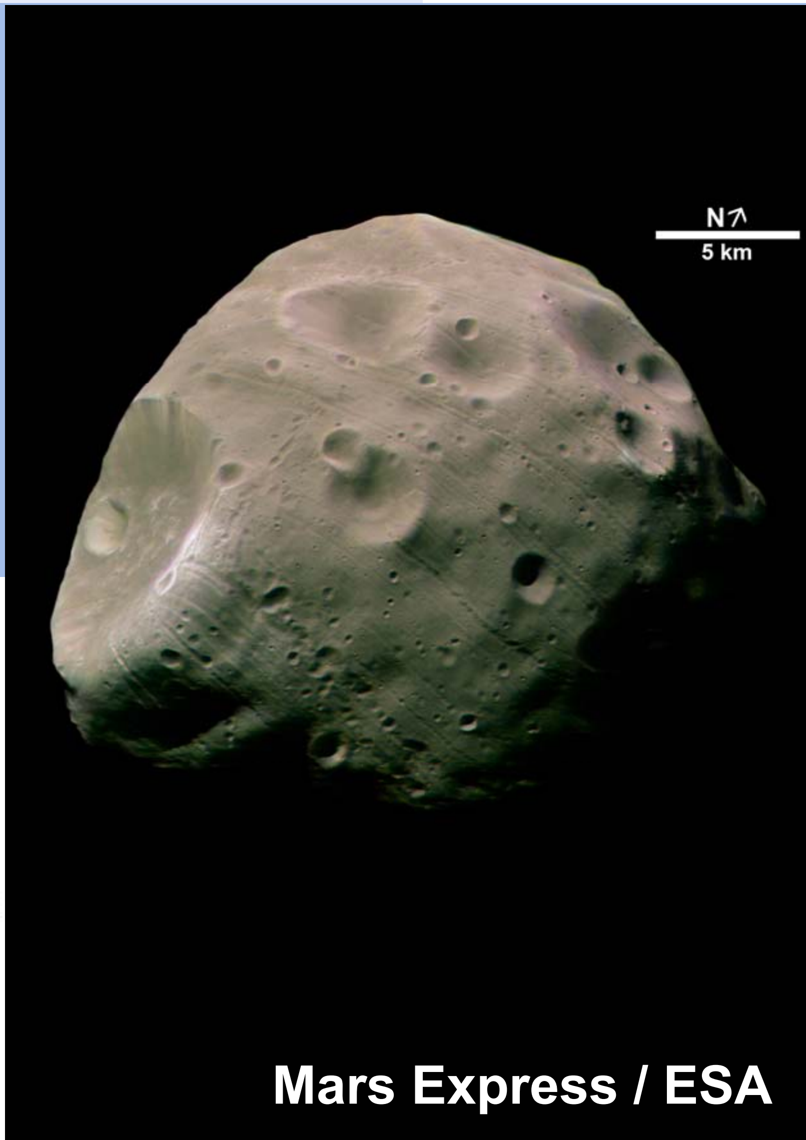
Phobos-Grunt (rus. Фобос-Грунт)

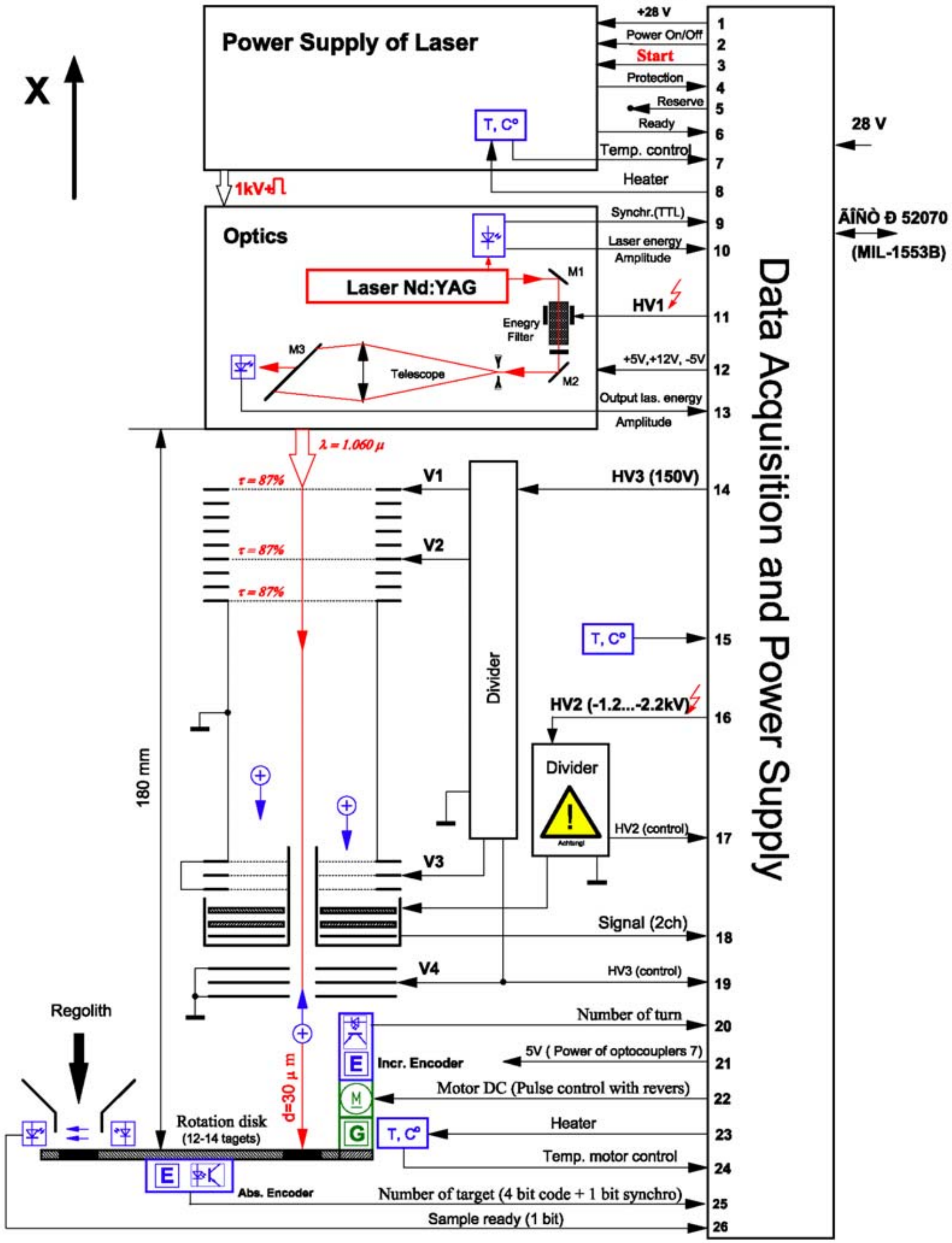
- Collect soil samples from Phobos and possibly from Mars and return them to Earth for scientific analysis.
- Phobos, Mars, and Martian space investigations.
- In situ and remote studies of Phobos, including analysis of soil samples.
- Monitoring the atmospheric behaviour of Mars, including the dynamics of dust storms.
- Studies of the vicinity of Mars, to include its radiation environment and plasma and dust.



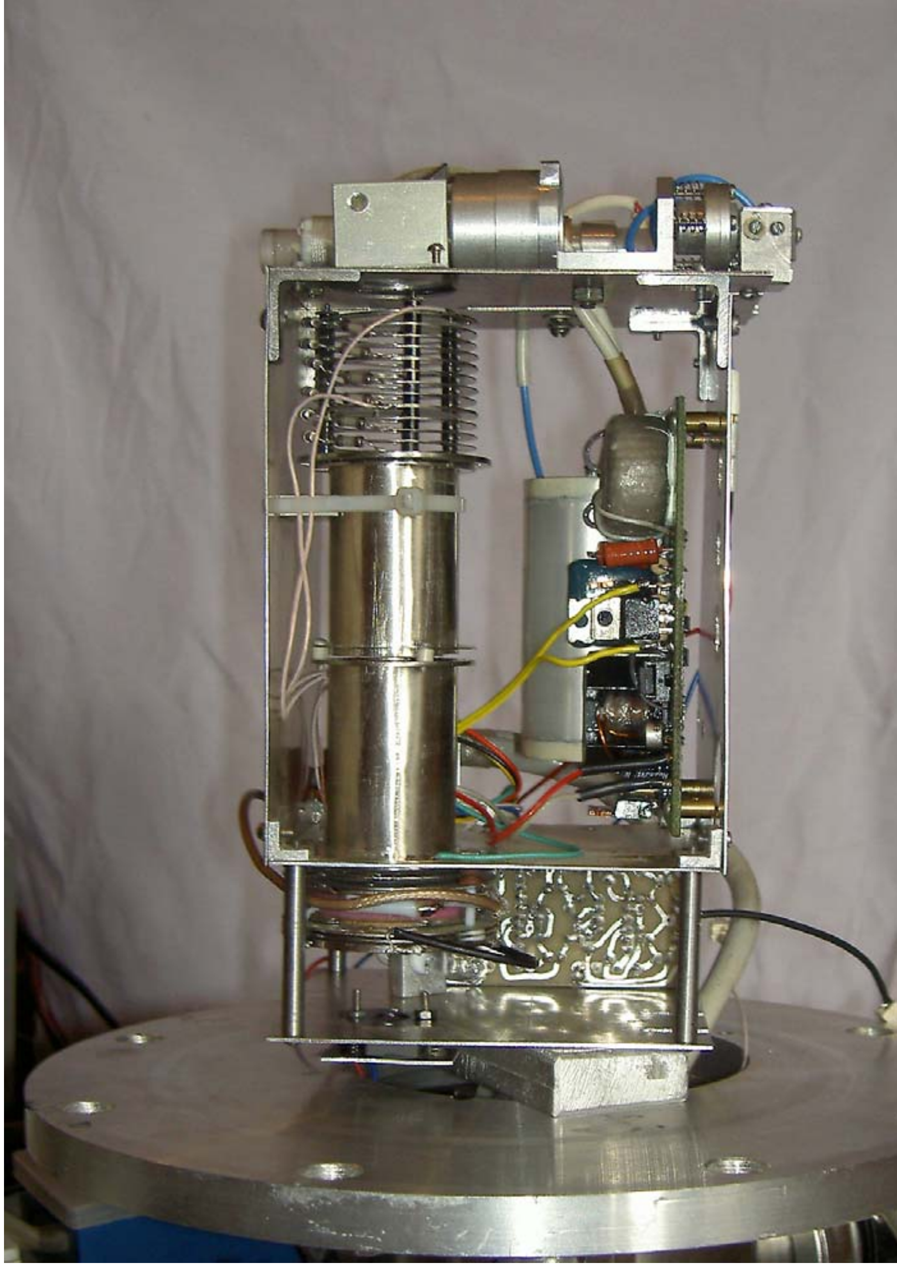


Phobos-Grunt Structural Model

LASMA Functional Blockdiagram

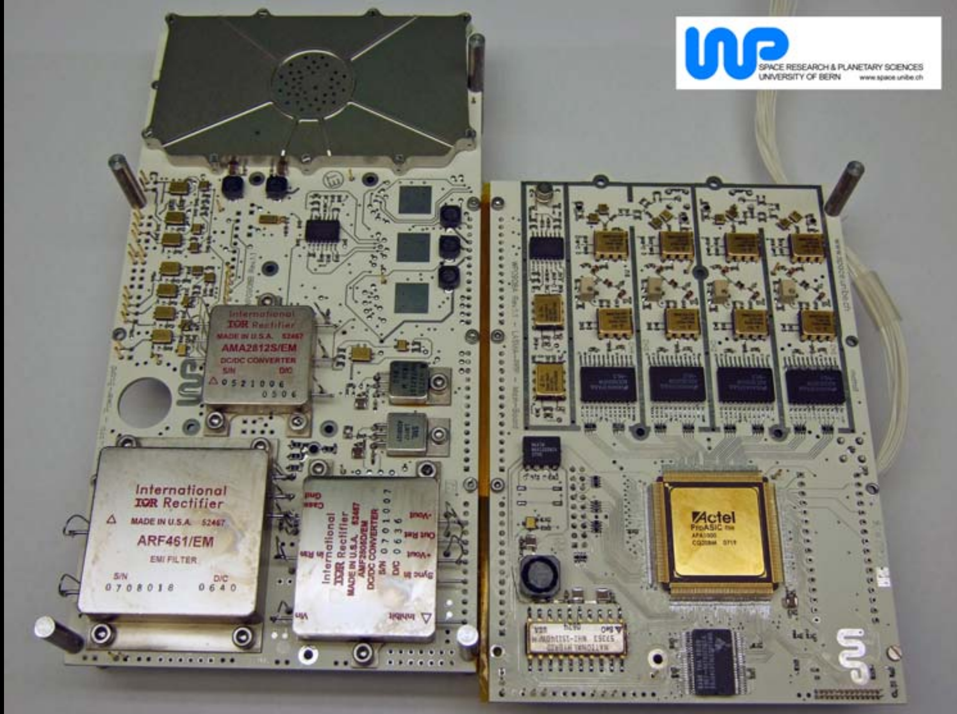


M,G - MAXON MOTOR (Motor and gearhead)



LASMA

PI: G.Managadze, IKI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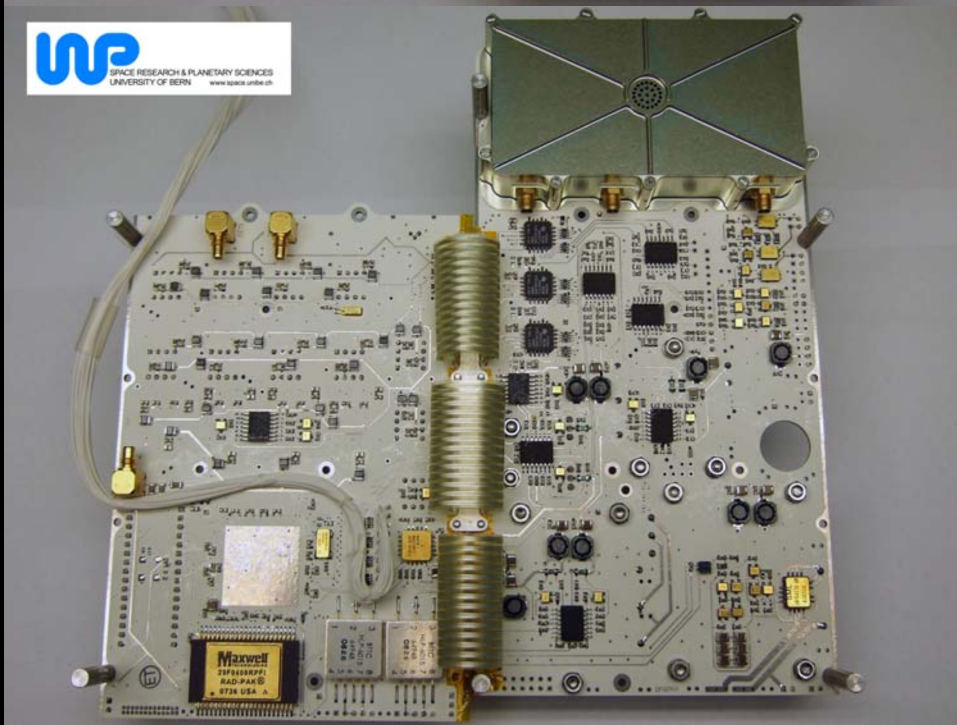
ProASIC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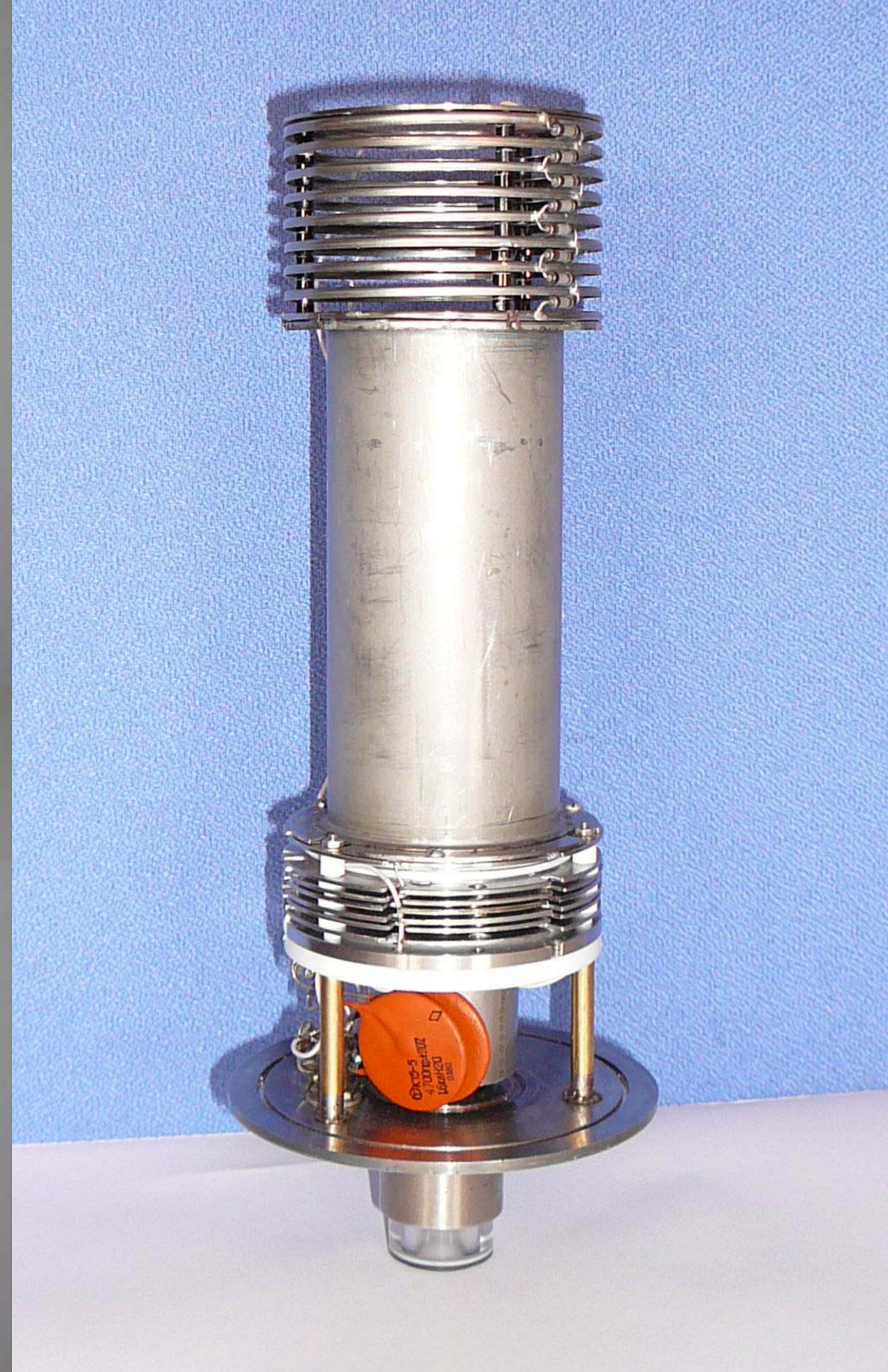
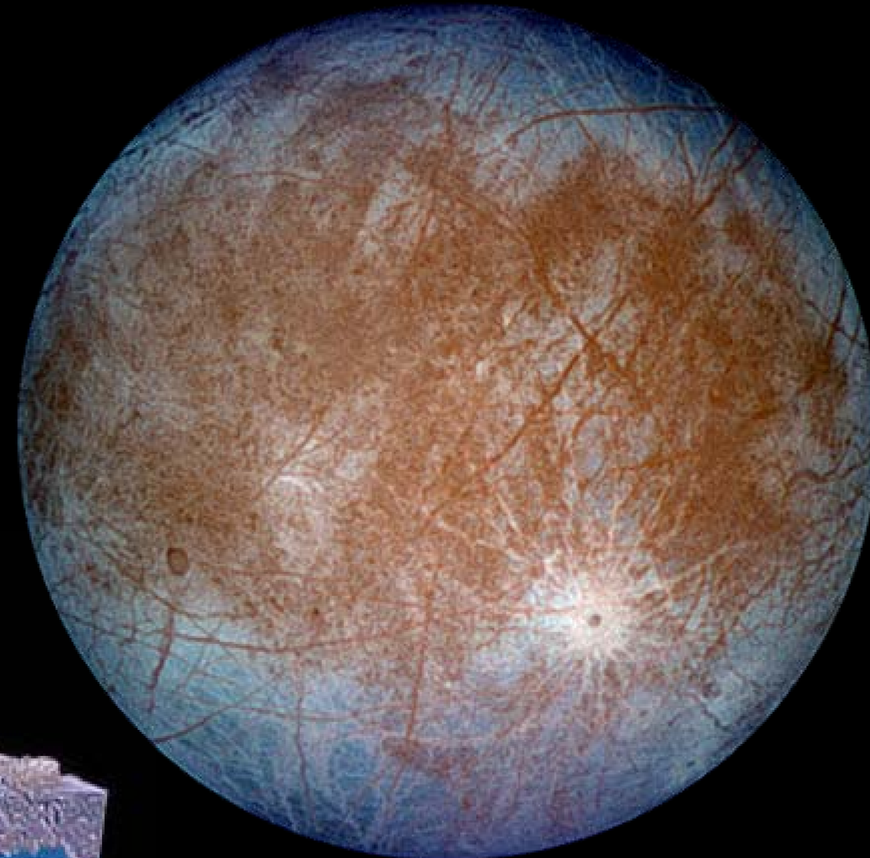
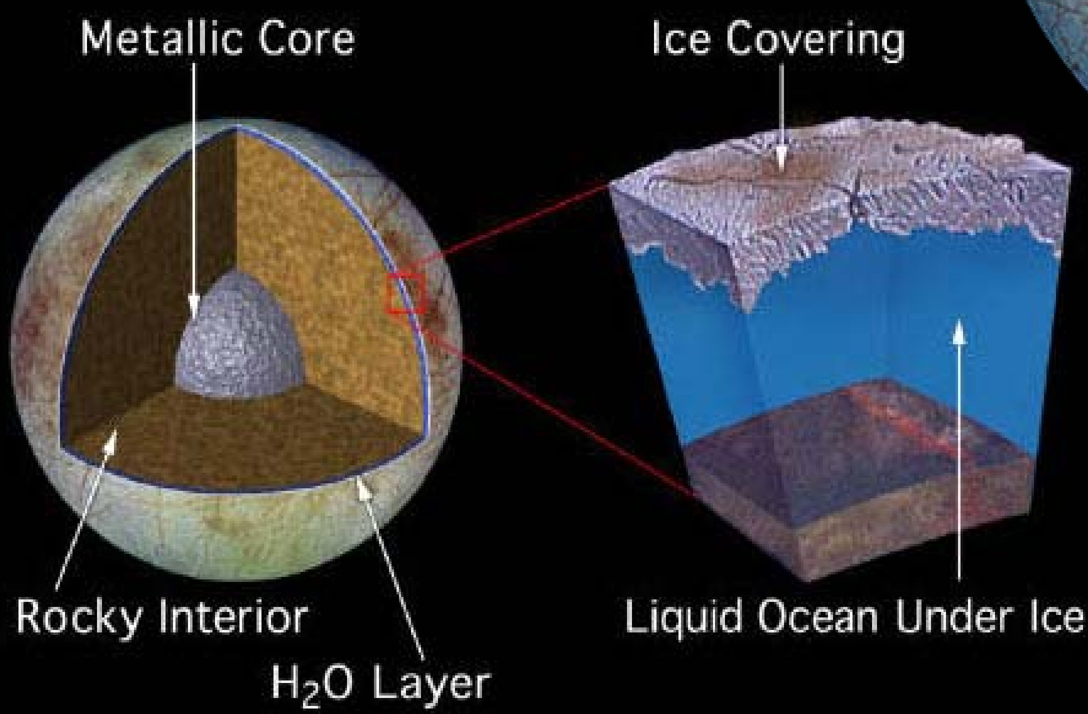


Europa / Jupiter



Gallileo / NASA



Europas Surface Composition

- Bright Areas (ice-rich regions)
  - H_20, CO_2,
  - SO_2, S_x,
  - H_2O_2, ...

- Dark Areas (ice-poor regions)
  - $MgSO_4 \cdot xH_20$
  - $Na_2SO_4 \cdot xH_20$
  - $Na_2CO_3 \cdot xH_20$
  - $H_2SO_4 \cdot xH_20$
- Possible extremophile bacteria
  - Cyanidium
  - Deinococcus radiodurans
  - Sulfolobus shibatae
  - Escherichia coli

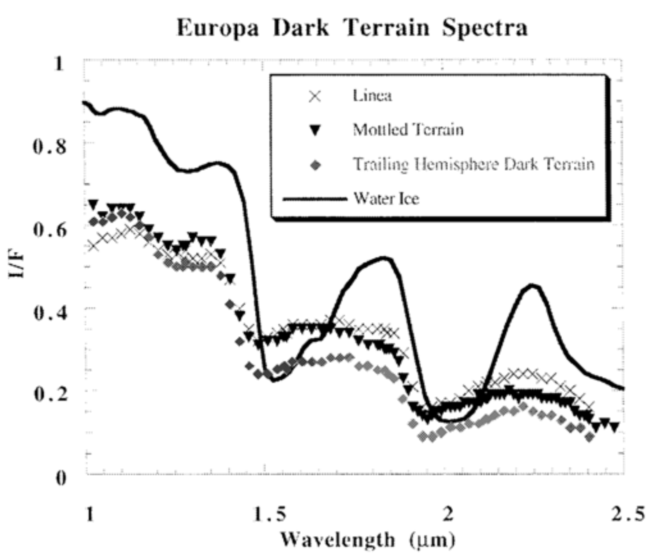


FIG. 2. This figure compares two NIMS spectral samples to a medium grained water ice spectrum (from Clark 1981). The size of the data point symbols are approximately equivalent to the error bars of the data. Notice how the Europa NIMS bandcenters are offset from the 1.5- and 2.0-μm water ice bandcenters. The linea spectral 3 × 3 element averaged sample was collected from the Europa 6 NIMS surface composition 2 observation from within the linea. The mottled terrain spectrum is a 5 × 5-element spectral average sample of mottled terrain from the Ganymede 1 orbit NIMS northern high latitude observation. The trailing hemisphere dark terrain spectrum 5 × 5 element averaged sample was obtained from the Europa 4 orbit NIMS surface composition 2 observation.

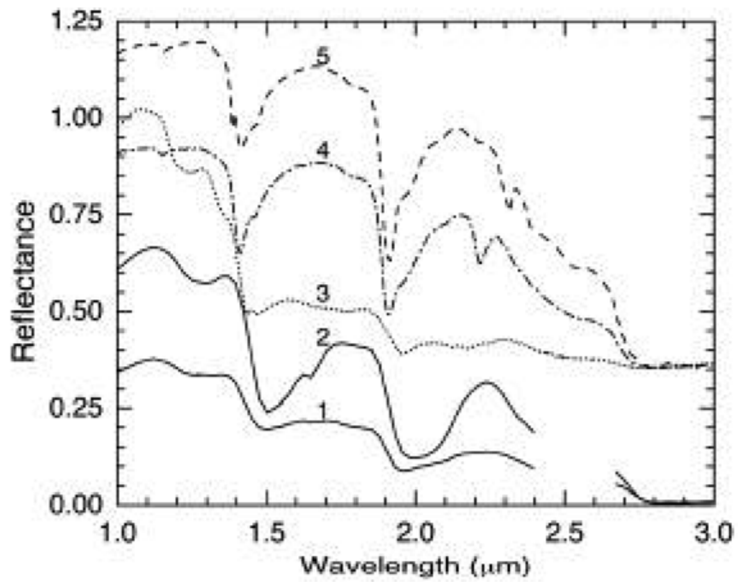


Figure 1. Reflectance spectra from the Galileo NIMS instrument are shown for Europa non-icy (1) and icy (2) areas. Spectrum (3) is for the salt mineral Hexahydrite [$MgSO_4 \cdot 6H_2O$] and shows very similar features; this is the prime candidate for the material composing much of the non-ice portion of the surface. Spectra (4) and (5) are for hydrated clay minerals Sepiolite [$Mg_4Si_6O_{15}(OH)_2 \cdot H_2O$] and Montmorillonite [$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_210(OH)_2 \cdot nH_20$], respectively. Clay minerals have been suggested as the non-ice constituent of Europa's surface, but clays do not have the broadened water features found for Europa. Further, clays have metal-OH absorptions in the 2.2 to 2.4-µm region which do not occur for Europa. The non-Europa spectra are offset by +0.35.

Biomarker Definition and Examples

Category/Definition	Examples
Category 1 – The property is indisputable evidence for life and has characteristics which cannot be produced by any known nonbiologic process either in nature or in the laboratory despite extensive attempts.	• Actual unambiguous living forms capable of metabolism, movement, and reproduction • Complex fossils such as trilobites or skeletons with indisputable morphologies (extremely difficult with single-cell life) • Hopanes (prokaryotic cell membrane residue)[1] • Steranes (eukaryotic cell membrane residue)[1] • Porphyrins (hemoglobin residue)[1]
Category 2 – The property is very strong evidence for life and is not likely to be produced by known nonbiologic processes, but is not indisputable.	• Traditional organic biomarkers used in the fossil fuel industry[2] • Magnetite produced by some magnetotactic bacteria[2] • Some extreme examples of carbon isotopic fractionation • Less intricate forms resembling known fossils, biofilm, mineralized microbes
Category 3 – The property is known to be produced by life but is also known to be produced by nonbiologic processes.	• Presence and enhancement of nitrogen, phosphorous • Ratios of certain elements such as phosphorous to uranium • Iron isotopic fractionation • Sulphur isotopic fractionation • Many fossil-like morphologies • Amino acids • Polycyclic aromatic hydrocarbons (degradation product of life, product of burning, etc.) • Micrometer-size spherical or ovoid objects • Many low temperature minerals • Specific mineral compositions and associations • Non-equilibrium coexistence or zoning in minerals

[1]Stable biomarker which may be used in the search for extinct life (survives on the order of 2.7 billion years).
[2]May potentially be Category 1 instead of Category 2

Variations in Isotopic Abundance: Carbon

$$\delta^{13}C = \left(\frac{\left({}^{13}C/{}^{12}C\right)_{\text{Sample}}}{\left({}^{13}C/{}^{12}C\right)_{\text{ref.}}} - 1 \right) \times 1000$$

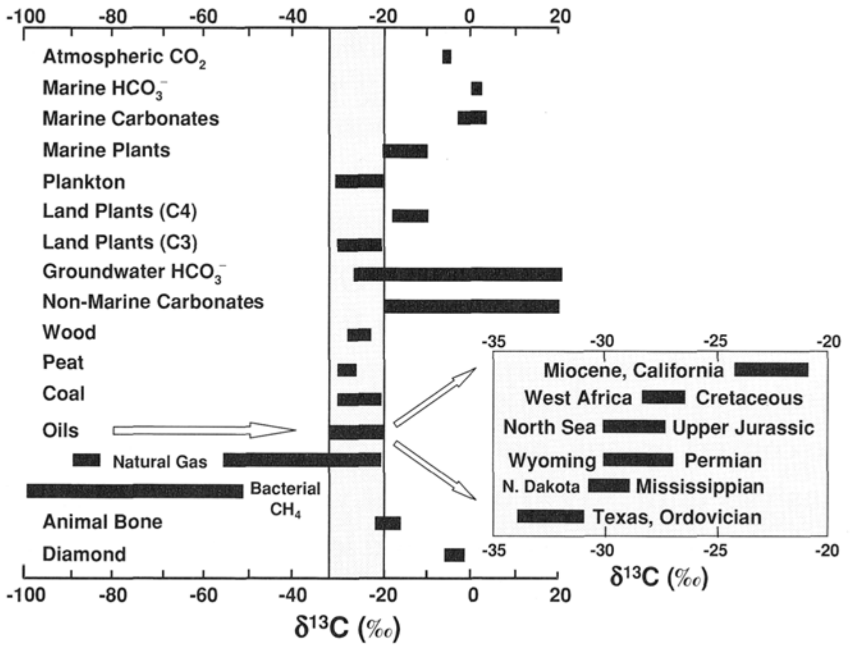


Figure 6.2. Variations in stable carbon isotope ratios (VPDB standard) for different organic and inorganic compounds (modified from Mook, 2001). C3 and C4 plants are discussed in the text. The expanded scale shows ranges of isotopic values for various crude oils from some petroleum source rocks, arranged from oldest at the bottom to youngest at the top. Stable isotope ratios can be used with biomarkers to show relationships between crude oils and their source rocks. Reprinted with permission by ChevronTexaco Exploration and Production Technology Company, a division of Chevron USA Inc.

The Biomarker Guide, K.E. Peters, C.C. Walters, and J.M. Moldowan, Cambridge, 2005

Sulphur Isotopes on Earth, Meteorites and Moon

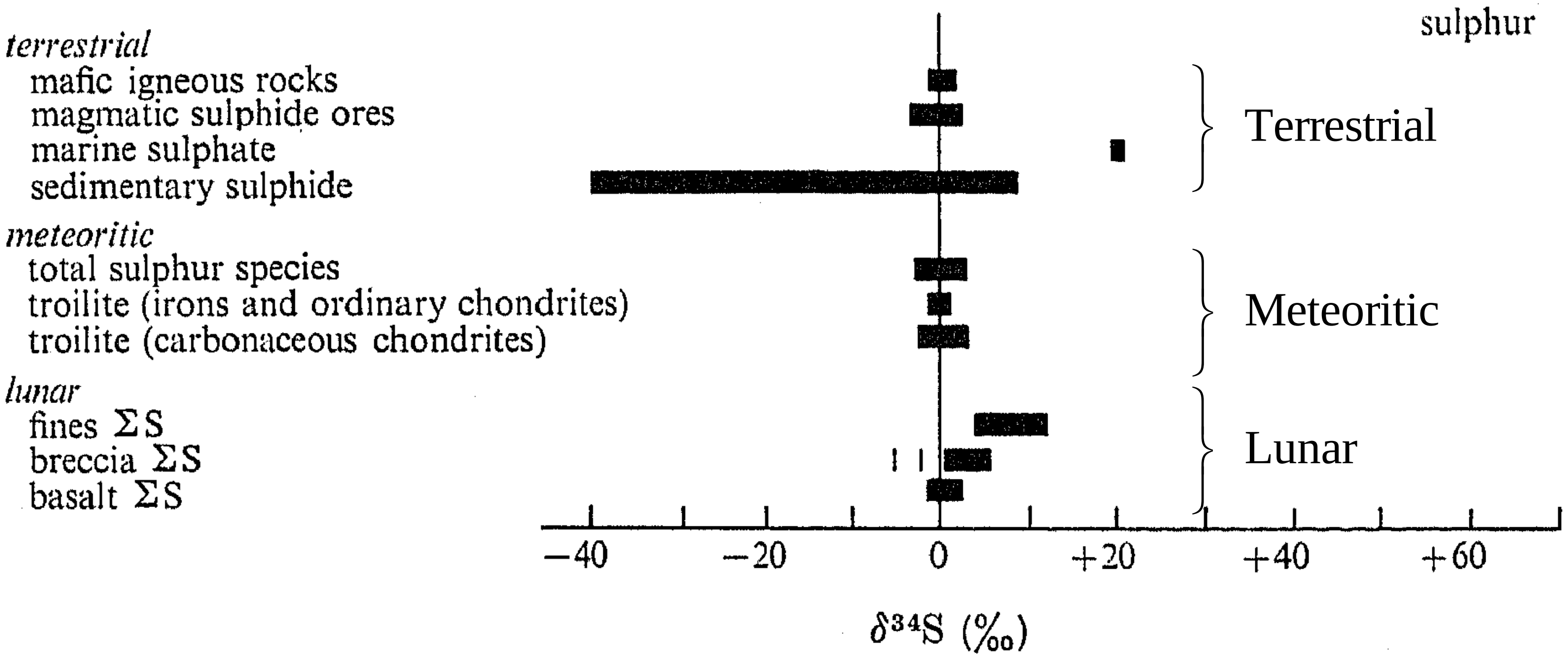


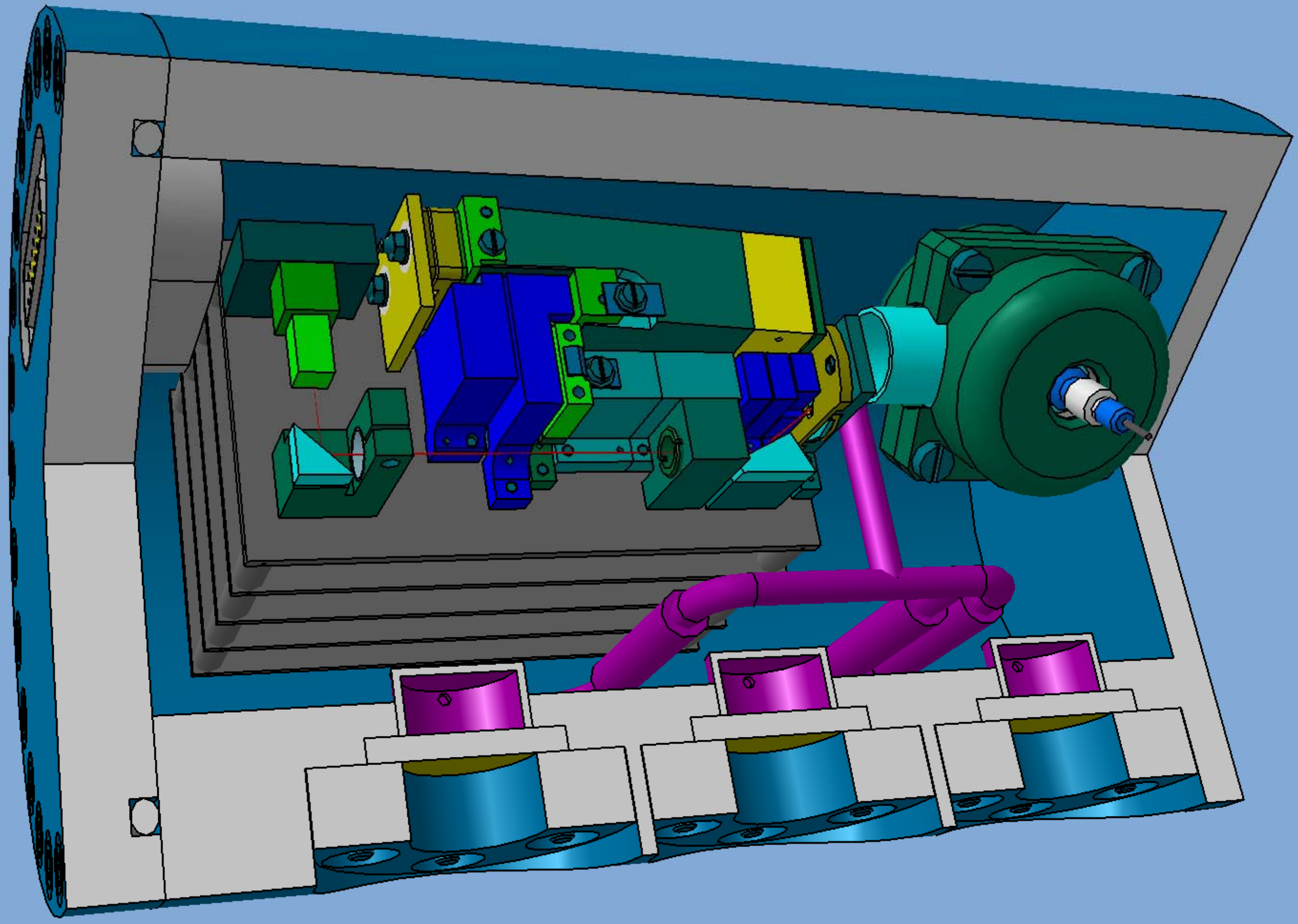
FIGURE 11. Distribution of $\delta^{13}C$ and $\delta^{34}S$ in terrestrial, meteoritic and lunar material (adapted from Kaplan, Smith & Ruth 1970).

$$\delta^{34}S = \left(\frac{\left({}^{34}S / {}^{32}S \right)_{\text{Sample}}}{\left({}^{34}S / {}^{32}S \right)_{\text{CDM}}} - 1 \right) \times 1000$$

Kaplan, I. R., Stable Isotopes as a Guide to Biogeochemical processes, Proc. R. Soc. Lond. B, 189, (1975) 183–211.

Membrane-Inlet Mass Spectrometer (MIMS)

MIMS instrument was designed for a thermal drill for a NASA mission study. Designed to work to 180 bars, e.g. the ice sheet thickness.



Conclusions

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- We developed two miniaturised laser mass spectrometers for planetary research (BepiColombo/MSE)
  - Lander LMS: Ø60 x 160 mm, 550 g, 3W / 8.5W
  - Rover LMS: 70 x 50 x 50 mm^3, 280 g, 3 W
- Upcoming application of an LMS instrument will be on the Phobos-Grunt mission
- Current development of ice surfaces similar to Europa
- Concepts developed for an instrument to be part of a melting probe payload
  - Europa
  - Mars pole
  - ...

Space Applications

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- Limited resources
  - Power
  - Volume
  - Mass
  - Data rate
- Autonomous operation
  - Simple instrument operation
- Environmental
  - Vibration, shock
  - Thermal
  - Acoustic
- Mission duration
- Radiation environment

Lander LMS Resources

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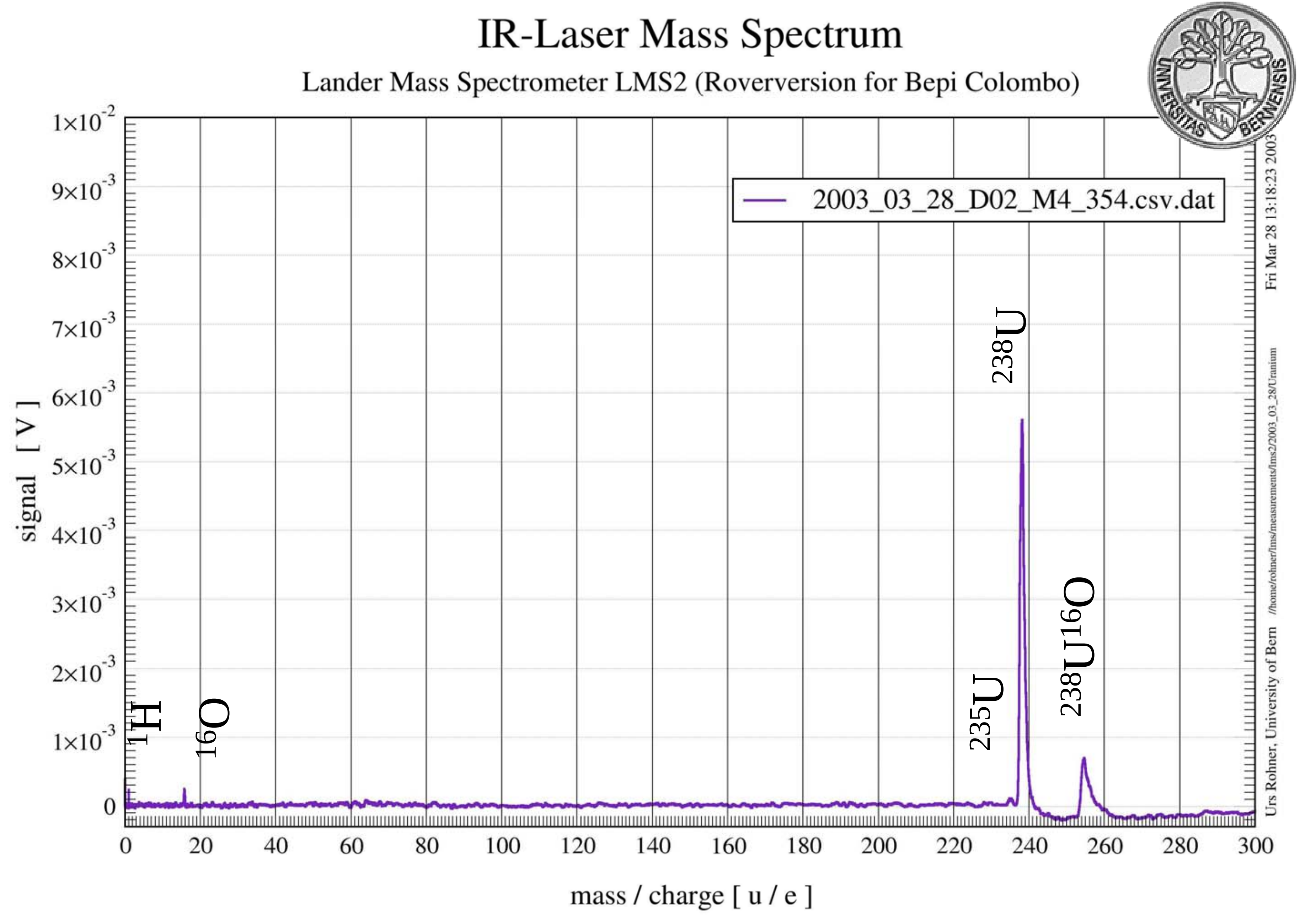
	Volume [mm^3]	Mass [gr]	Power [mW]
Ion optics	Ø60 x 160	150	—
HV electronics	—	30	50 / 50
Laser electronics	—	40	500 / 2900
Digital Interface	40 x 50 x 10	20	150 / 200
Data acquisition	100 x 100 x 25	190	1700 / 3100
DPU	70 x 80 x 20	70	500 / ≤2000
Harness	4 x 1 m	50	
Total		550	2900 / 8250


IR-Laser Mass Spectrum
Lander Mass Spectrometer LMS2 (Roverversion for Bepi Colombo)
2003_03_28_D02_M4_354.csv.dat
signal [V]
mass / charge [u / e]
1H
16O
235U
238U
238U16O
Fri Mar 28 13:18:23 2003
Urs Rohner, University of Bern
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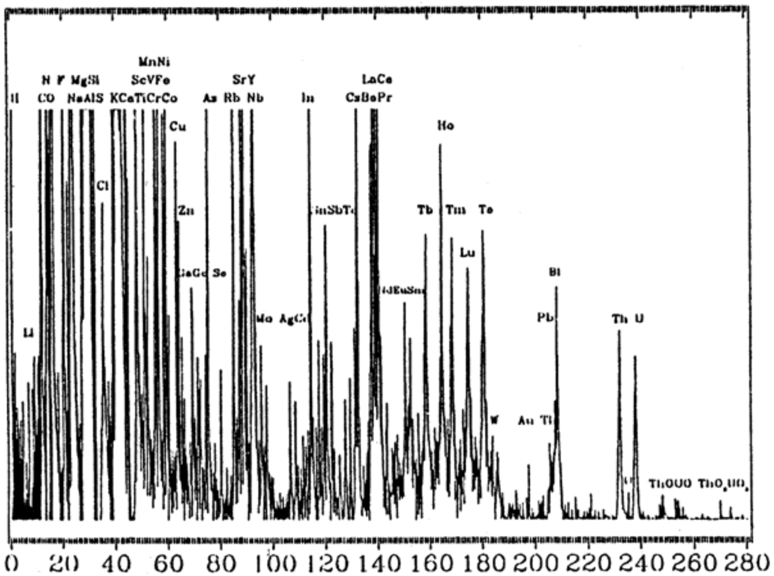
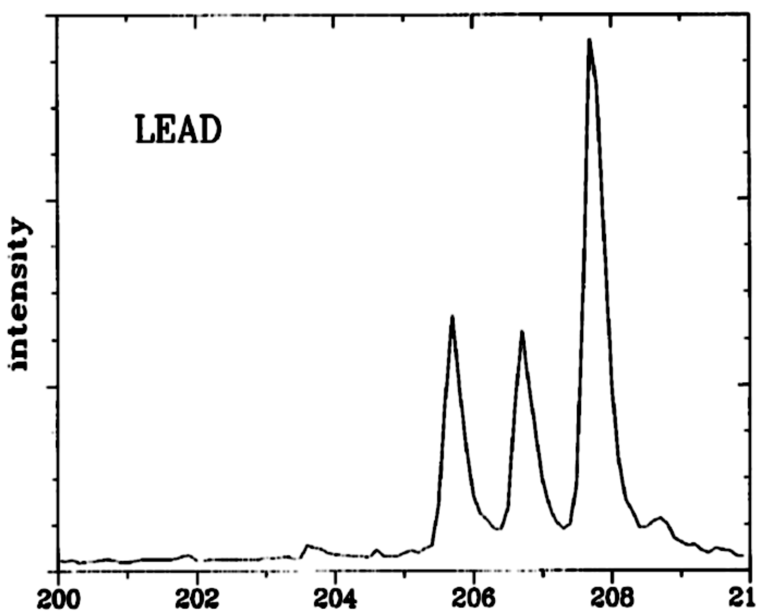
Resources of Rover LMS Flight Design

Mechanical dimensions	Sensor 70 x 30 x 40 mm^3, including electronics and laser system
Mass	Sensor 280 g overall
Mounting location	Sensor entrance deployed to planetary ground by pointing compartment entrance onto object
Mass range	1–300 amu
Mass resolution	$m/^{2} m = 180$
Power	Standby 200 mW, operation average 3 W, peak 5 W

NBS Glass Matrix SRM 610 (single shot)





Concentration in % weight		
Element	LASMA analysis	Reference
Au	84.68	84.5
Pt	7.12	6.9
Pd	4.30	5.0
In	1.22	1.75
Ag	1.10	1.0
C	2.5×10^{-3}	2×10^{-3}
Fe	0.49	0.7
H	0.31	N/I
Zn	0.13	0.15
Re	0.65 Max	0.1