



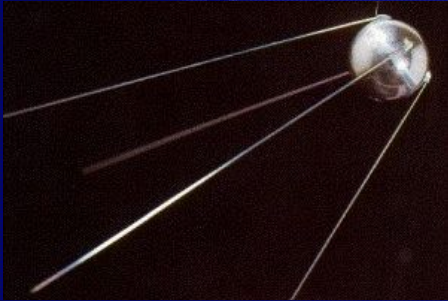
# Mass spectrometry in the history of the solar system exploration

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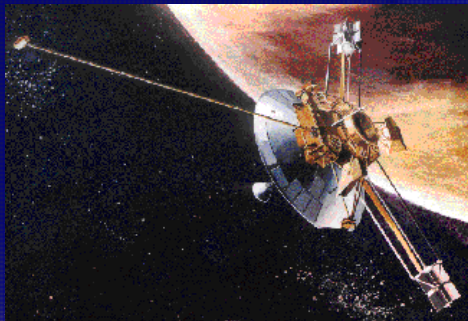
# Space exploration at a glance



**1957** : first artificial satellites (Sputnik 1 & 2)



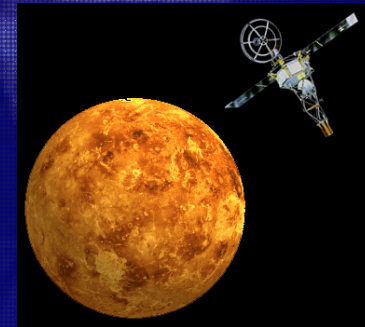
**1961** : first human in space (Gagarine)



**1972** : first probe launched to the outer solar system (Pioneer 10)



**1969** : first human on the moon (Armstrong)



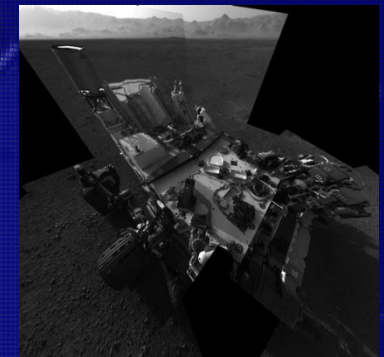
**1962** : first interplanetary probe success (Mariner 2, Venus)



**1986** : first long term space station in Earth orbit (MIR)



**1995** : first orbital probe of the outer solar system (Galileo, Jupiter)



**2012** : first one ton rover outside the Earth system



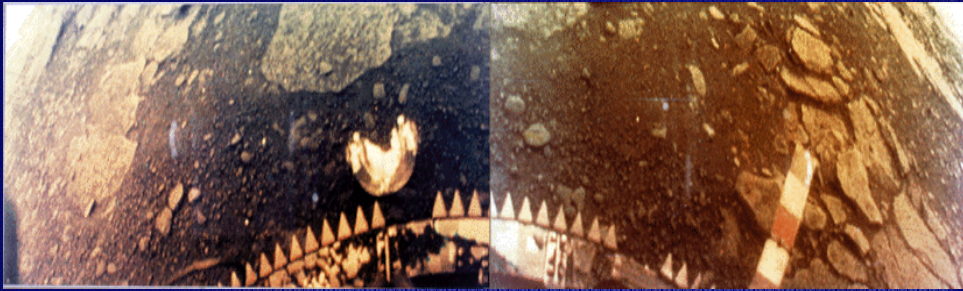
**1976** : first MS on another planet



# Why sending space probes to explore other worlds ?

Remote sensing by spectroscopy is the primary tool for exploring the solar system **BUT**

1. Limited to observable environments



*Venus surface as seen by Venera probes*



*Salts revealed by the Mars Exploration Rovers*

2. Not suited to measure everything

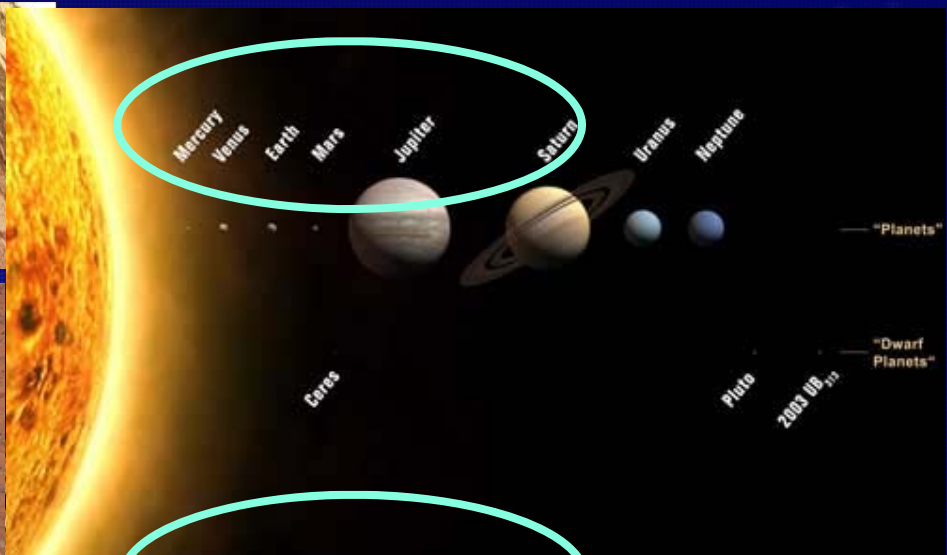
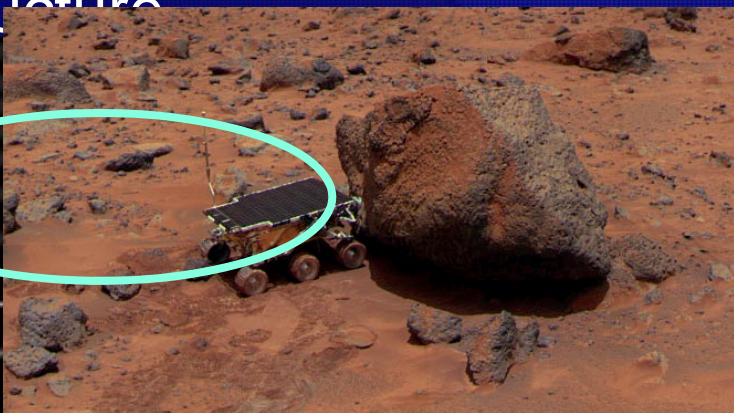
- Magnetic fields
- Noble gases
- ...



# Main goals of in situ exploration



Structure



C  
M  
S  
R

Pluto

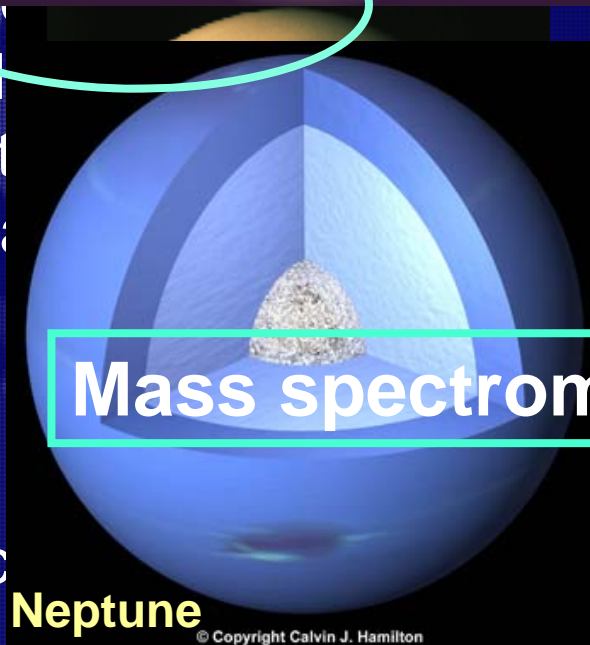
Magnetohull

Heat up to 10 times  
thicker than of Earth



ACTIV

s specific



Neptune

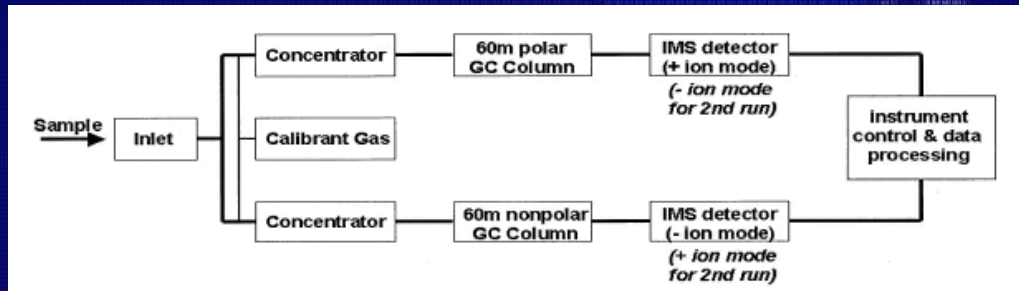
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# Mass spectrometry in space : what for ?

## Two applications :

1. Air monitoring (VOCs) in inhabited spacecrafts and stations (Apollo, MIR, ISS)



*Principle scheme and picture of the VOA system used in the US shuttle to monitor the ambient air*



2. Exploration of solar system environments : chemical composition (detect and count various neutrals and ions)



# Challenges for in situ mass spectrometry

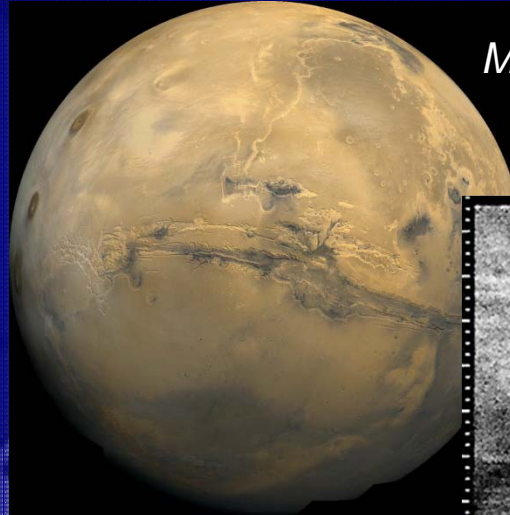
Property	Space	Laboratory
Weight	~kg	10-100 kg
Power	~10-50 W	100-1000 W
Size	<50 cm	1-10 m
Robustness	10g @ 100 Hz	1g
	Thermal cycling	Isothermal conditions
	Space radiation	
Data volume	~100 Mo max.	No limitation
Contamination	You carry what is on/in the spacecraft	Cleaning/Sterilization
Sampling	Aaaarghhh !	“Easy”



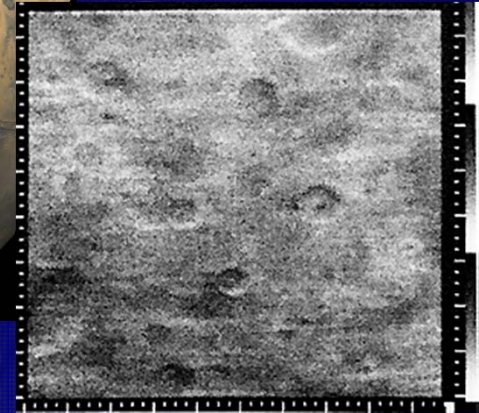
# The Viking mission to Mars (1976) : first safe landing on another planet

## Interest of Mars :

1. Not too far from Earth
2. Telluric planet
3. Believed to host life



*Mars & 1st picture of its surface  
returned by Mariner 9 probe*



*Picture of a Viking lander replica with C. Sagan*

## Viking probe & objectives :

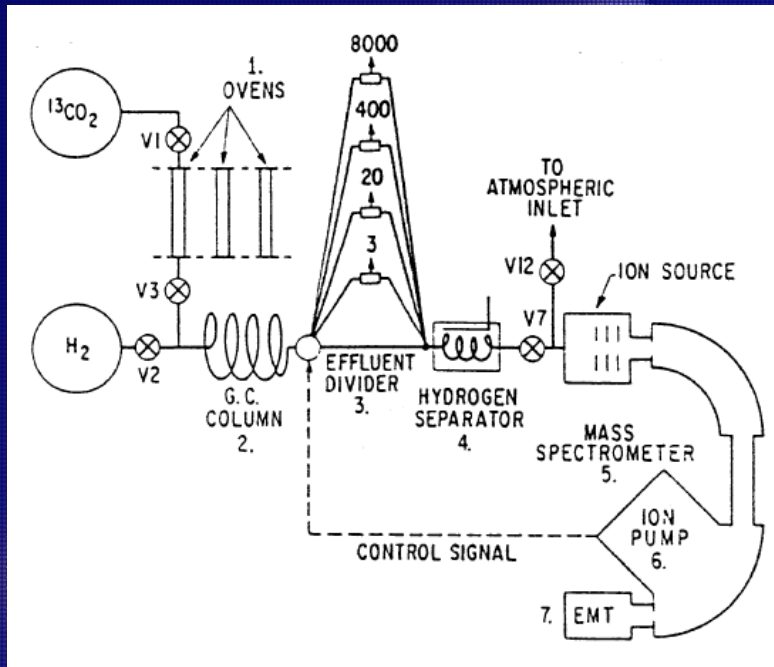
1. Lander (~700 kg)
2. Atmosphere and surface composition
3. Search for life



# The Viking mission to Mars (1976) : first (GC-)MS in an alien world to seek the first aliens

## The GC-MS experiment : all in one !

1. Atmosphere analysis (direct MS)
2. Soil analysis (GC-MS)
3. Label Released experiment analysis (GC-MS)



*GC-MS experiment scheme*  
(Biemann et al., 1976)

## MS main specifications :

Nature :	Double sector (E/B)
Mass :	~22 kg
Volume :	~20 cm <sup>3</sup>
Power :	140 W
m/z range :	12-250
Sensitivity :	ppbv-ppmv (soil)



# The Viking mission to Mars (1976) : good atmospheric measurement...

## First complete atmospheric composition:

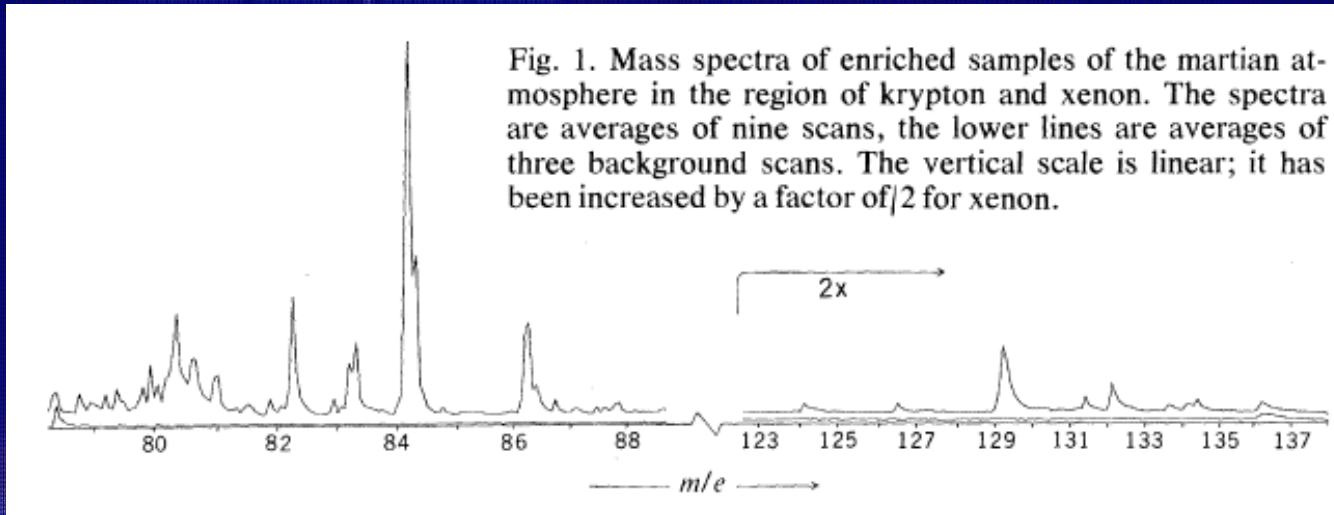


TABLE 1. Composition of the Lower Atmosphere

Gas	Proportion
Carbon dioxide (CO <sub>2</sub> )	95.32%
Nitrogen (N <sub>2</sub> )*	2.7%
Argon (Ar)*	1.6%
Oxygen (O <sub>2</sub> )	0.13%
Carbon monoxide (CO)	0.07%
Water vapor (H <sub>2</sub> O)	0.03%†
Neon (Ne)*	2.5 ppm
Krypton (Kr)*	0.3 ppm
Xenon (Xe)	0.08 ppm
Ozone (O <sub>3</sub> )	0.03 ppm†

\* Discovered by Viking experiments.

† Variable.

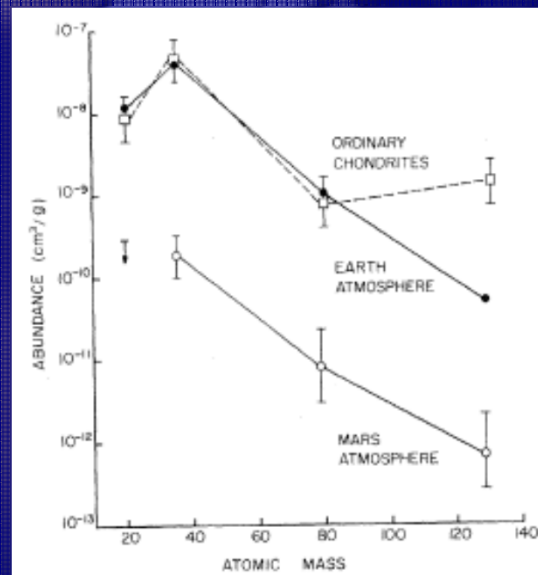


TABLE 2. Isotope Ratios in Atmospheric Gases

Ratio	Earth	Mars
<sup>12</sup> C/ <sup>13</sup> C	89	90
<sup>18</sup> O/ <sup>16</sup> O	499	500
<sup>14</sup> N/ <sup>15</sup> N	277	165
<sup>40</sup> Ar/ <sup>36</sup> Ar	292	3000
<sup>129</sup> Xe/ <sup>132</sup> Xe	0.97	2.5

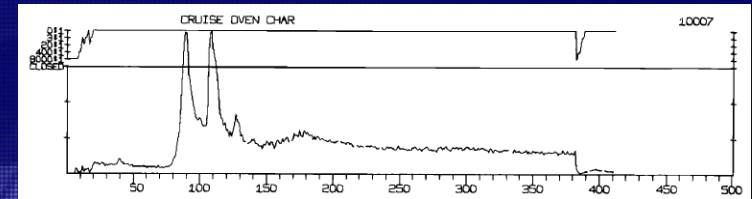
Uncertainties in the Mars values are presently ±10% except for Ar and Xe (see text).



# The Viking mission to Mars (1976) : ...but no alien (?)

No organic detected=no life (but...) :

Material	Quantity (temperatures in degrees Celsius)
<b>I. Inorganic</b>	
Carbon dioxide	Some in all experiments (quantitation not yet available)
Water	Sample 1: at 200°, much less than 0.1% at 500°, 0.1 to 1.0% Sample 2: at 350°, 0.1 to 1.0% at 500°, somewhat less than at 350°
<b>II. Organic</b>	
	None detected (see Table 3 for detection limits)
<b>III. Terrestrial contaminants</b>	
Methyl chloride	~ 15 ppb
Fluoroethers	1 to 50 ppb



*GC-MS dry run in flight (blank)*

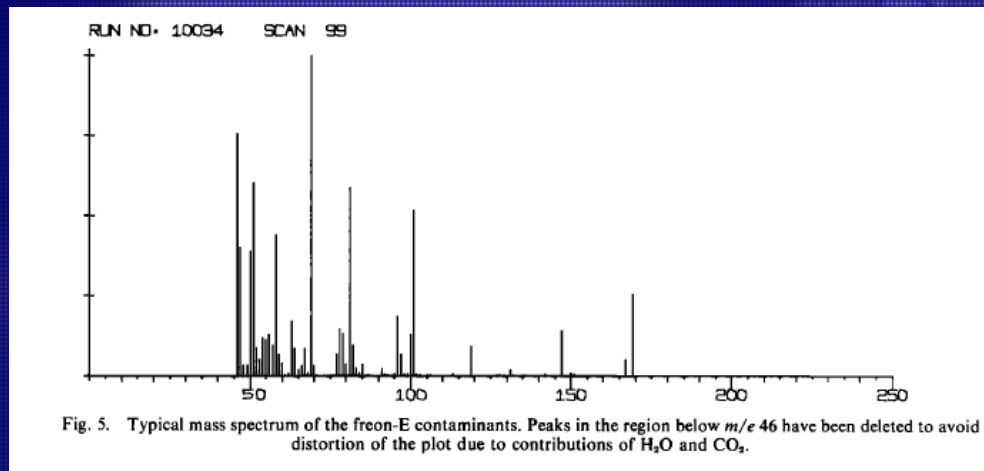


Fig. 5. Typical mass spectrum of the freon-E contaminants. Peaks in the region below  $m/e$  46 have been deleted to avoid distortion of the plot due to contributions of  $H_2O$  and  $CO_2$ .

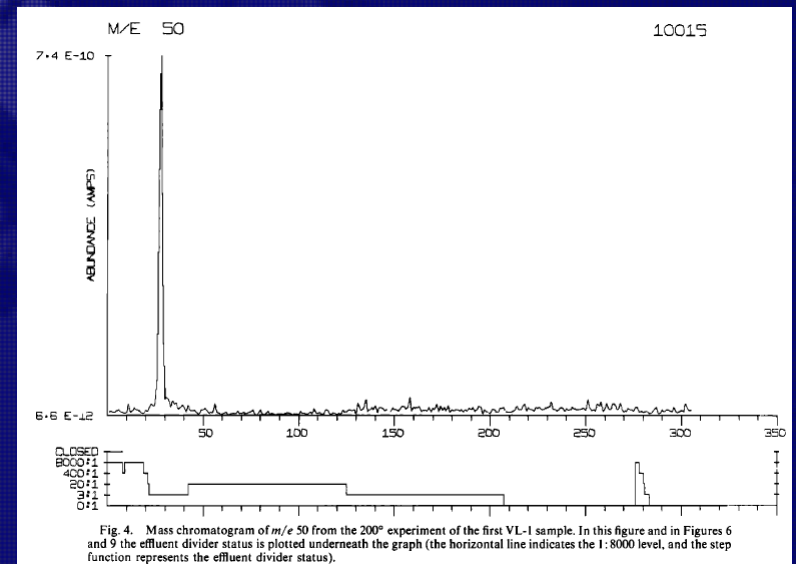


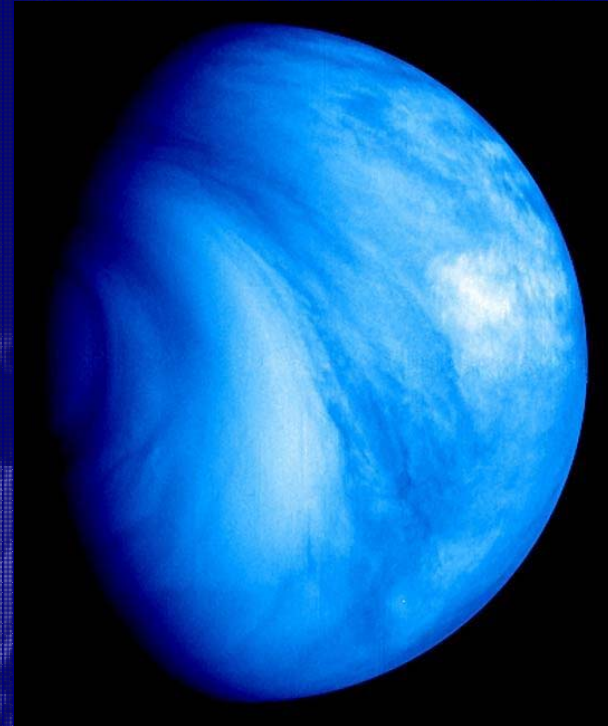
Fig. 4. Mass chromatogram of  $m/e$  50 from the 200° experiment of the first VL-1 sample. In this figure and in Figures 6 and 9 the effluent divider status is plotted underneath the graph (the horizontal line indicates the 1:8000 level, and the step function represents the effluent divider status).



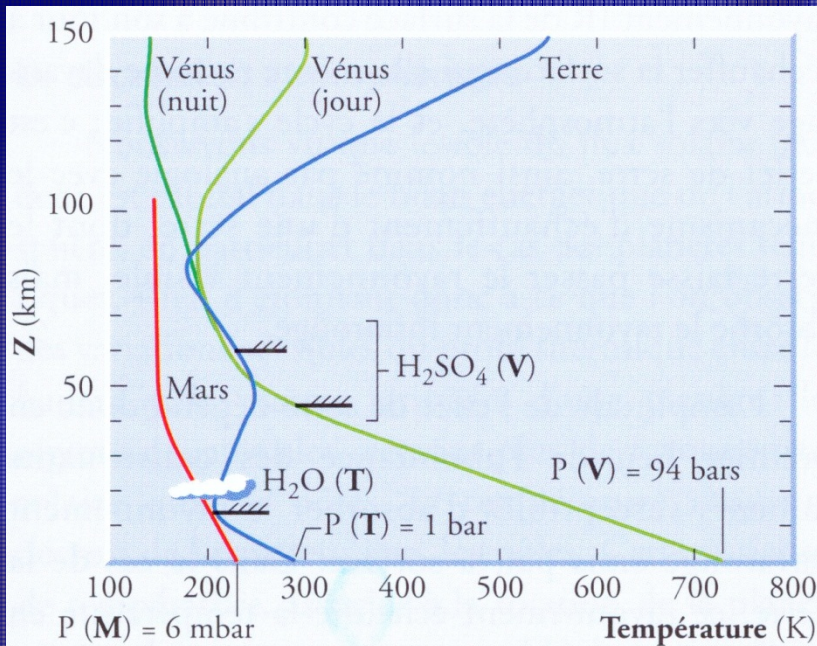
# Everybody goes to Venus !

## Interest of Venus :

1. Not too far from Earth
2. Telluric planet
3. Very dense atmosphere



*Picture of Venus from the venus express probe*



## Challenges :

1. Temperature
2. Pressure



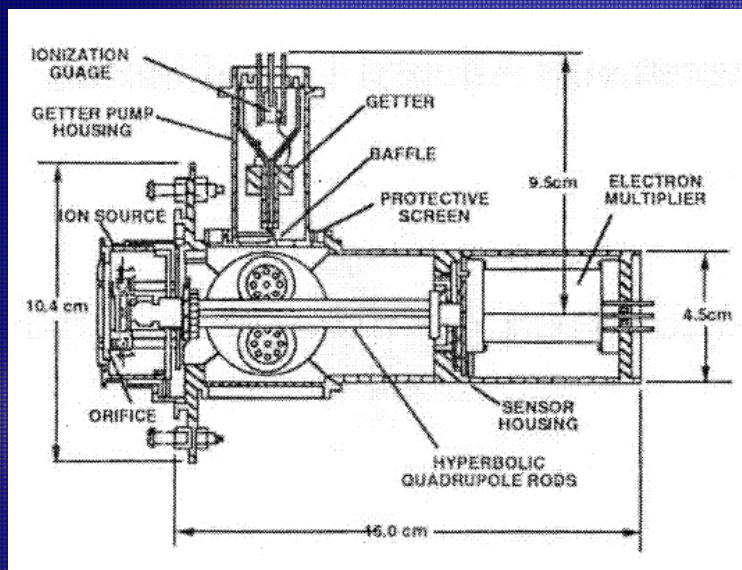
# The Pioneer-Venus mission to Venus (1978) : Atmosphere of Venus properties

Pioneer-Venus :  
5 atmospheric probes,  
2 onboarding a MS



*Artist view of  
Pioneer-Venus*

## 1. Upper atmospheric probe MS



*Scheme of the MS of the upper  
atmosphere probe (Niemann et al., 1980)*

## MS main specifications :

Nature :	Quadrupole
Mass :	~4 kg
Volume :	~20 cm <sup>3</sup>
Power :	12 W
m/z range :	1-46
Sensitivity :	N/A



# The Pioneer-Venus mission to Venus (1978) : Atmosphere of Venus properties

## First composition of the thermosphere

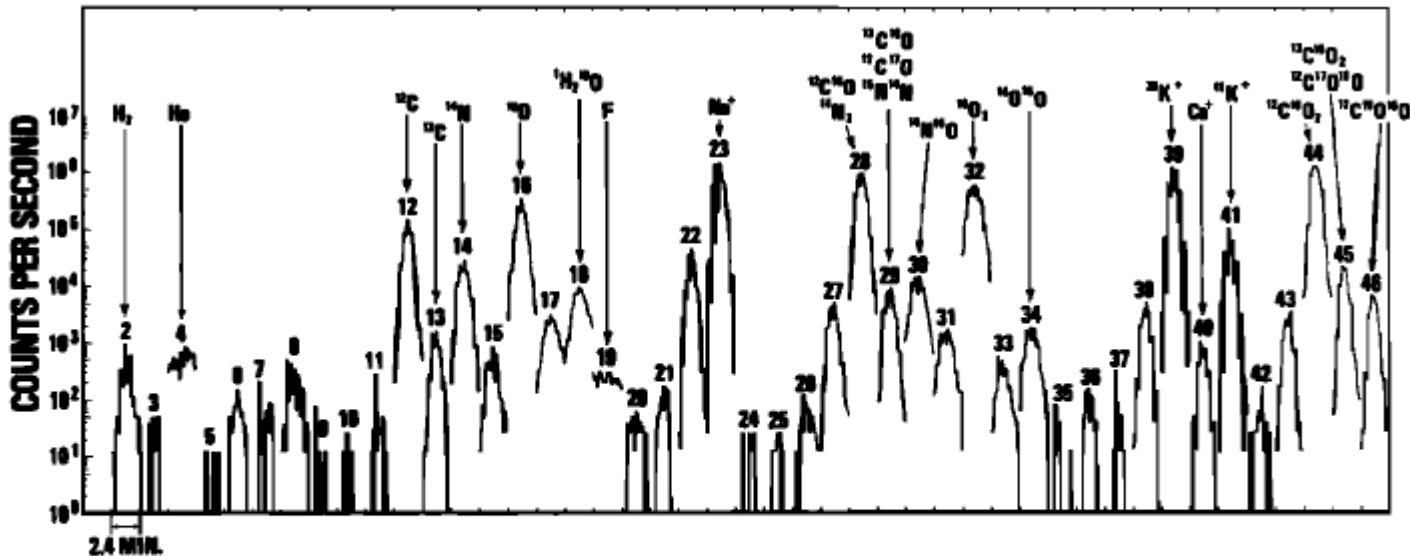
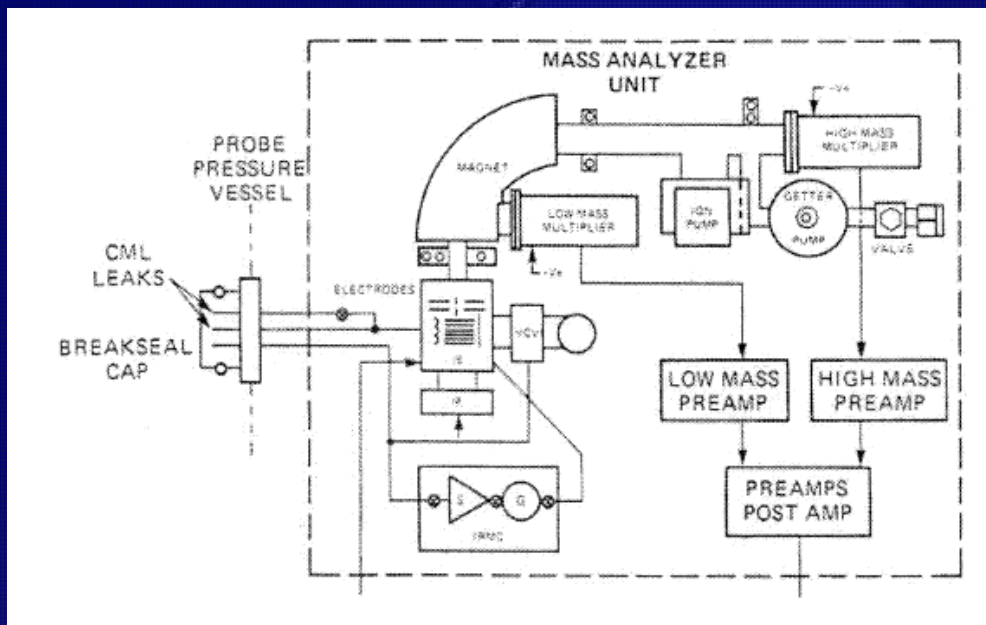


Fig. 3. Summary of the pulse counts measured at  $\pm 1.2$  min about periapsis for orbit 85 when the instrument was in the unit mass peak stepping mode. Starting on the left of each 2.4-min time interval marked on the abscissa the altitude is 161 km on the ingoing leg. After passing through periapsis altitude at 141 km the interval ends at 160-km altitude on the outgoing leg. The mass numbers are shown above each trace and some constituents are noted. Doubly charged ions, e.g.,  $\text{CO}_2^{++}$  or  $\text{Ca}^{++}$ , appear in the mass 22 and 20 trace.  $\text{Na}^+$ ,  $^{39}\text{K}^+$ ,  $^{41}\text{K}^+$ , and  $\text{Ca}^+$  are contaminants sputtered off the ion repeller grid by the  $\text{CO}_2$  flux.



# The Pioneer-Venus mission to Venus (1978) : Atmosphere of Venus properties

## 2. Lower atmospheric probe MS



*Scheme of the MS of the lower atmosphere probe  
(Niemann et al., 1980)*

## MS main specifications :

Nature : Sector (B)

Mass : ~12 kg

Volume : ~N/A

Power : 14 W

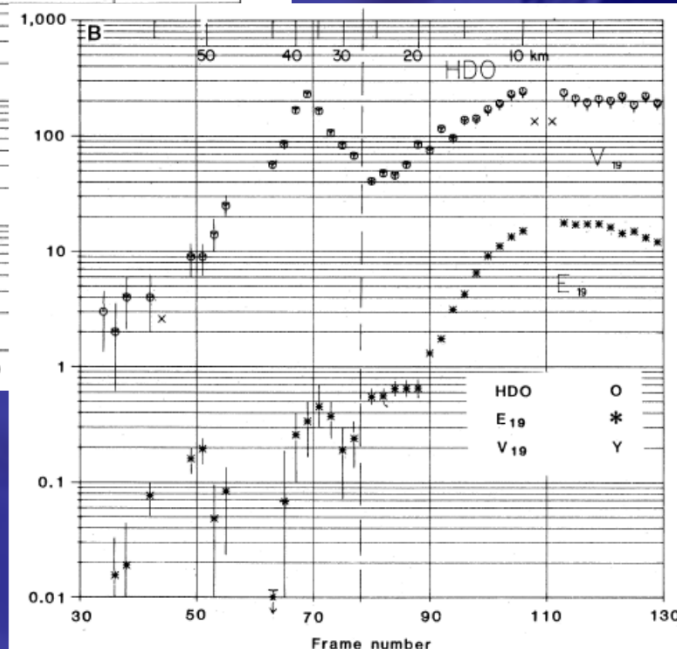
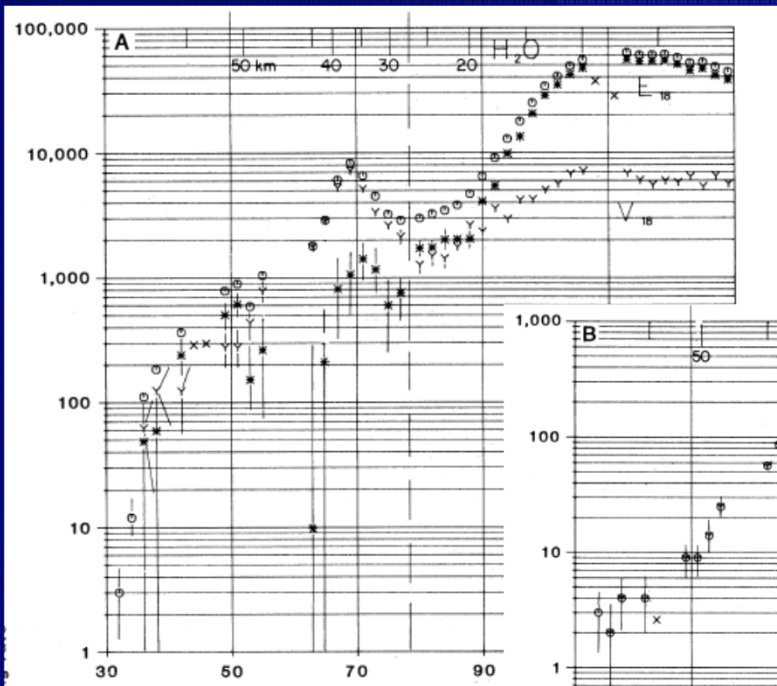
m/z range : 1-208

Sensitivity : ppmv

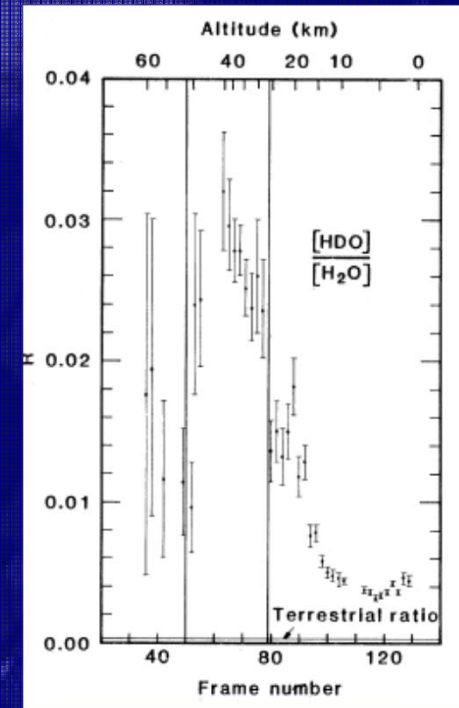


# The Pioneer-Venus mission to Venus (1978) : Atmosphere of Venus properties

Venus was wet in the past (and a large amount of water is now in the atmosphere)



Measurement of the amount of H<sub>2</sub>O and HDO during the descent



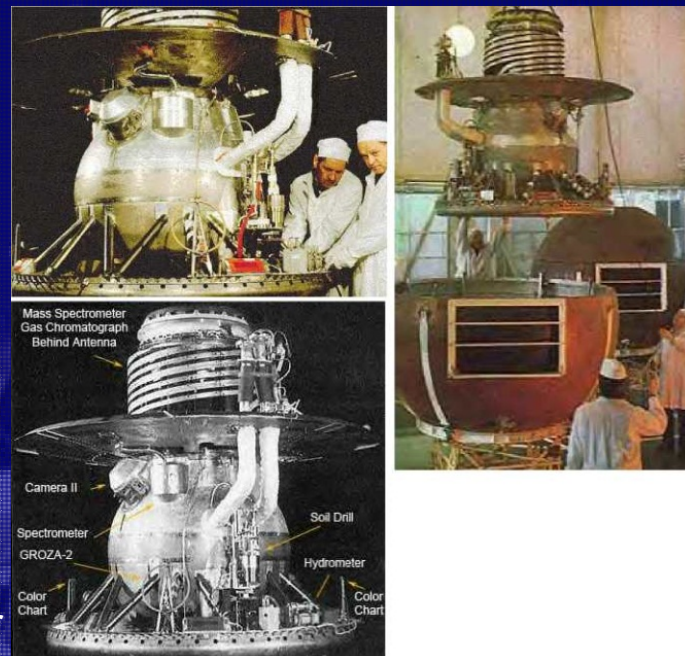
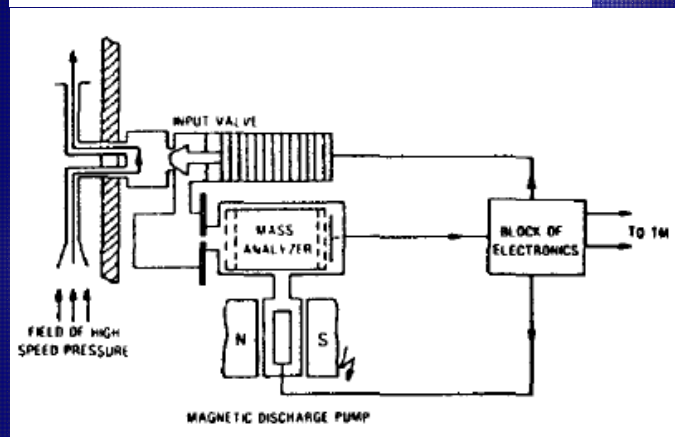
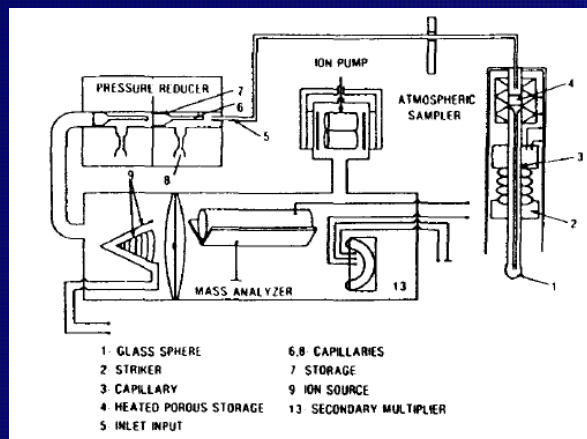
HDO/H<sub>2</sub>O ratio



# The Venera missions (1975-1978)

Venera : For each mission,  
1 orbiter and 1 lander

## Mass spectrometer onboard the landers



Picture of the Venera lander

## MS main specifications :

Nature : Monopole or Bennett RF  
 Mass : ~9.5 kg  
 Volume : ~N/A  
 Power : 17 W  
 m/z range : 11-105  
 Sensitivity : ~ ppmv



# The Venera missions (1975-1978)

First complete atmospheric composition (with GC analysis):

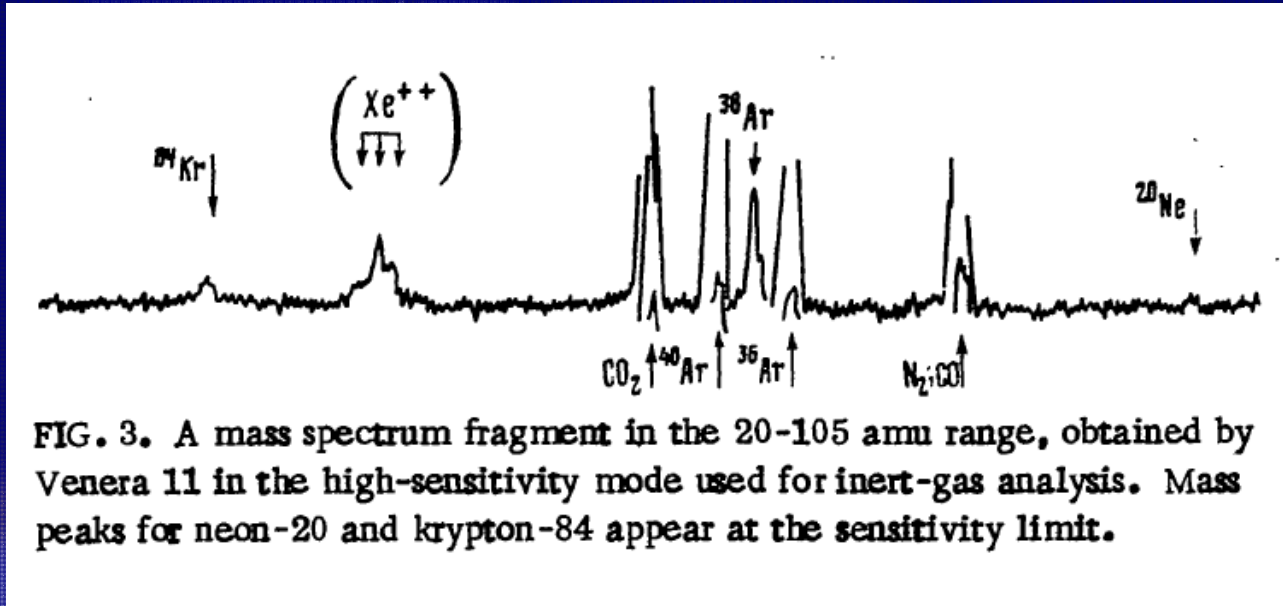


FIG. 3. A mass spectrum fragment in the 20-105 amu range, obtained by Venera 11 in the high-sensitivity mode used for inert-gas analysis. Mass peaks for neon-20 and krypton-84 appear at the sensitivity limit.

Species	Concentration ratio
CO2	95.5%
N2	4.5%
Ar	150 ppm
Ne	10 ppm
Kr	0.5 ppm



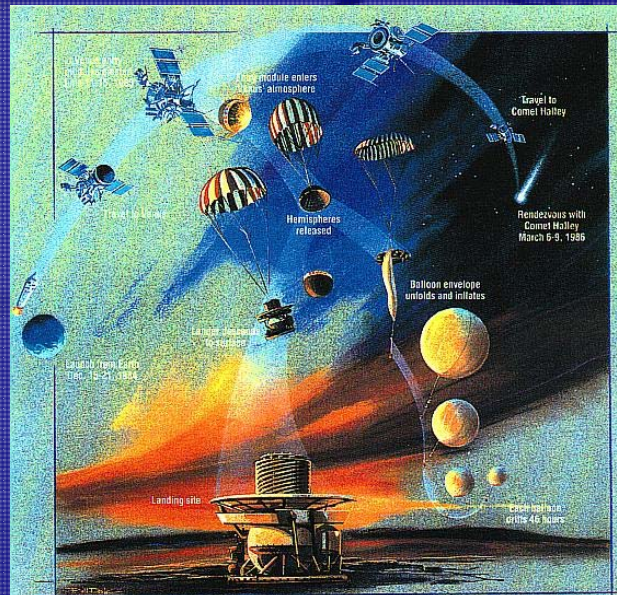
# First cometary exploration (1986) : first step of EU in space exploration

## Interest of comets :

1. Solar system/ISM link
2. Early history of the solar system
3. Origins of atmosphere/life



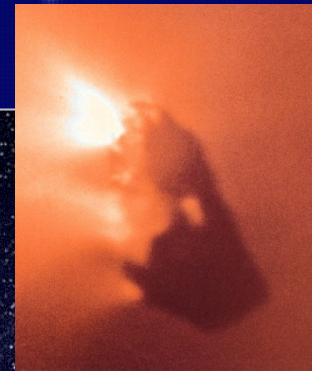
ESA Giotto probe



VEGA program



Comet P/Hale-Bopp



Comet Halley  
nucleus

## Two space missions devoted to study the Halley comet :

1. Giotto ESA probe
2. Vega russian probe



# First cometary exploration (1986) :

## first step of EU in space exploration

2 MS for the analysis of the neutral (NMS/DFMS) and ionized (IMS/Sector (B)) cometary atmosphere (not detailed here) onboard Giotto

MS for dust composition analysis onboard Giotto (PIA) and Vega (PUMA) Interest of comets :

### MS main specifications :

Nature : Time of Flight (TOF)

Mass : ~9.5 kg

Volume : ~N/A

Power : 17 W

m/z range : 11-105

Sensitivity : ~ ppmv

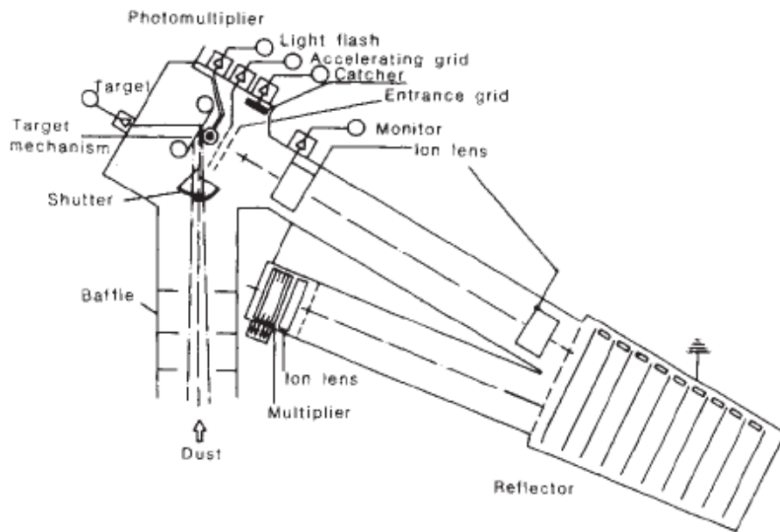
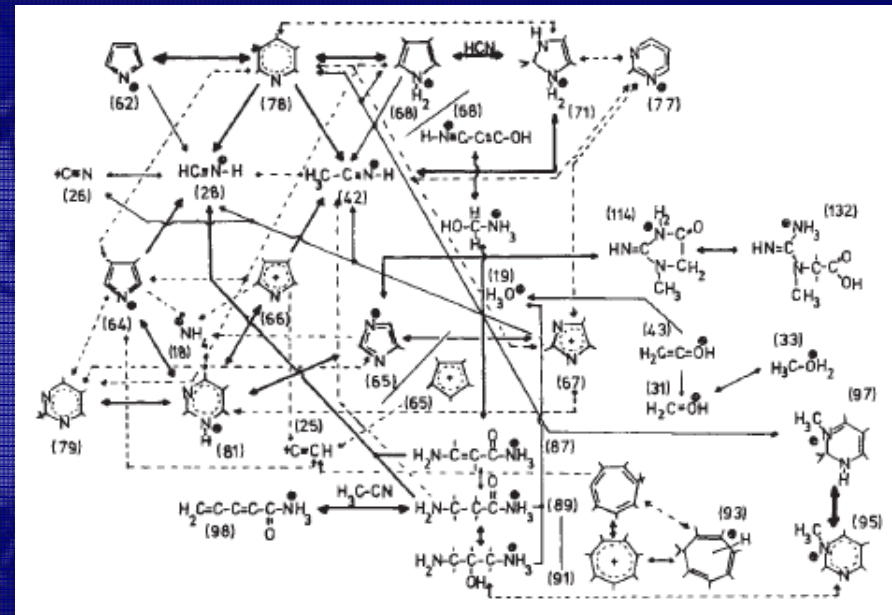
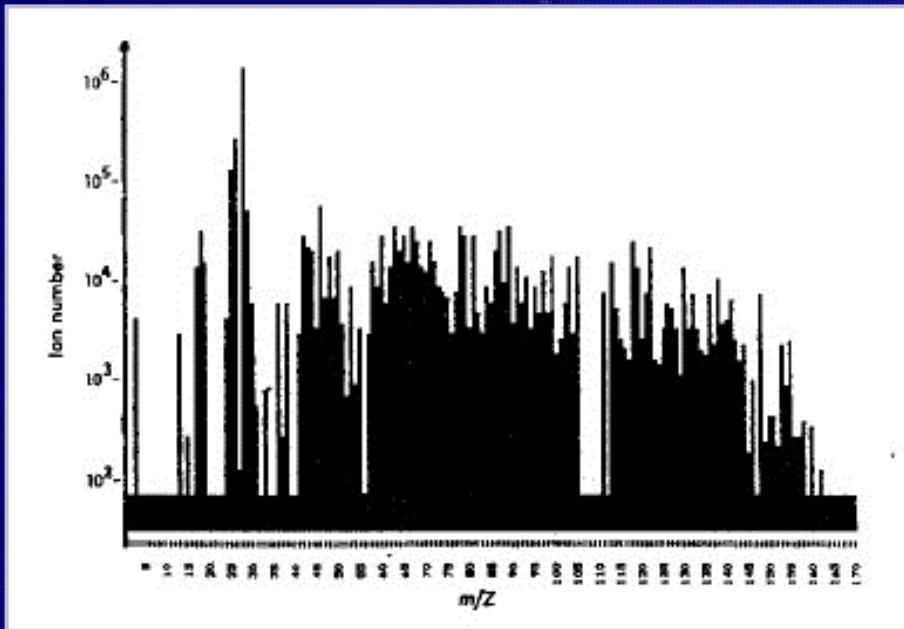


Fig. 1 The time-of-flight mass spectrometer analysing the ions released during the impact of dust particles.



# First cometary exploration (1986) : first step of EU in space exploration

Comets are really rich in organic materials !



*Mass spectrum recorded by PUMA-1 MS in-situ in the coma of comet P/Halley*

Presence of complex solid organic compounds in the grains  
BUT identification remains speculative



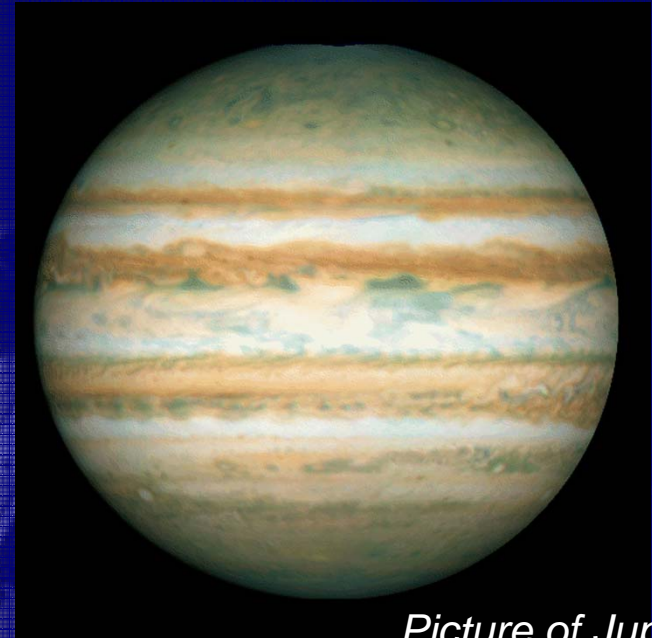
# Exploration of the Jupiter system with the Galileo mission (1995)

## Interest of Jupiter :

1. Biggest gaseous giant
2. Solar system origin
3. System of satellites
4. Similarity with exoplanets



*Artist view of the Galileo probe descent*



*Picture of Jupiter*

## Galileo probe & objectives :

1. Atmospheric probe (340 kg)
2. Composition of the upper atmosphere
3. Dynamics



# Exploration of the Jupiter system with the Galileo mission (1995)

## The GPMS experiment for the atmospheric composition analysis

*Pictures of GPMS*

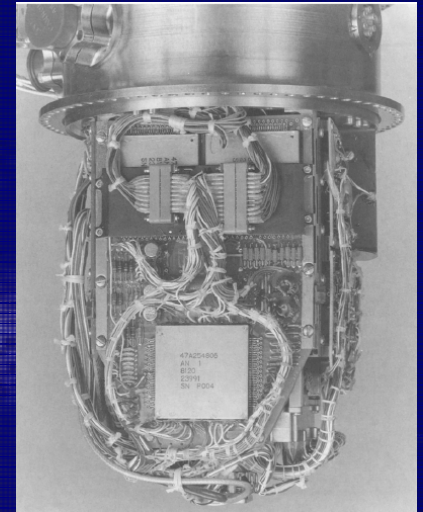
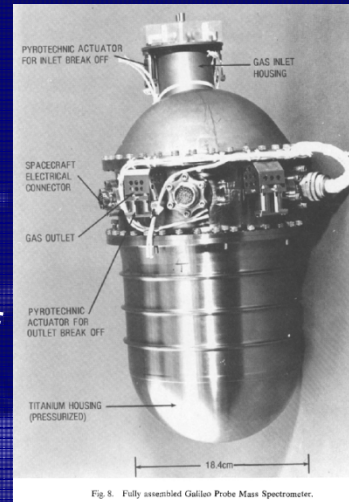
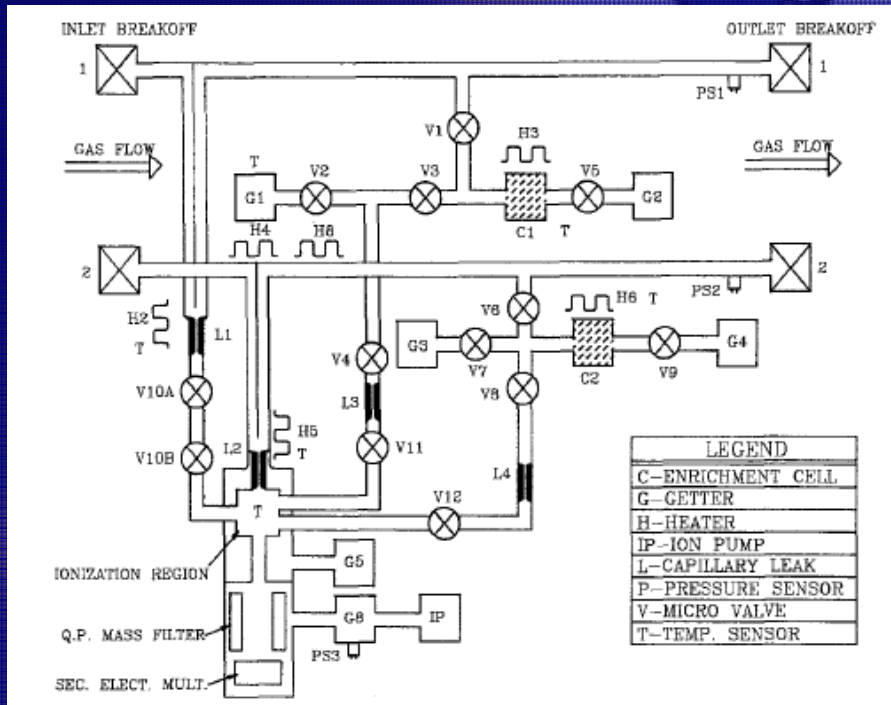


Fig. 8. Fully assembled Galileo Probe Mass Spectrometer.



*Scheme of the GPMS*

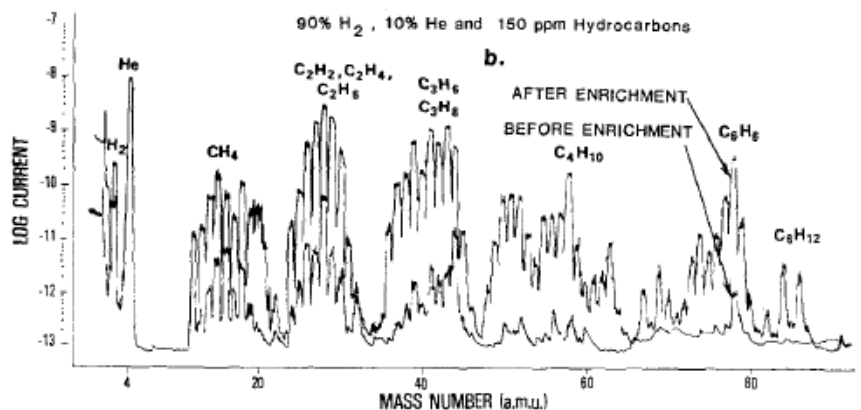
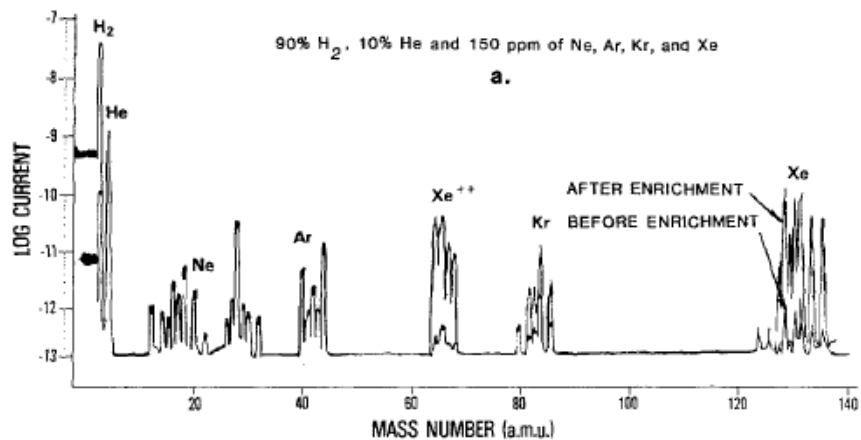
## MS main specifications :

Nature : Quadrupole  
 Mass : ~12 kg  
 Volume : ~ 3000 cm<sup>3</sup>  
 Power : 26 W  
 m/z range : 2-150  
 Sensitivity : N/A

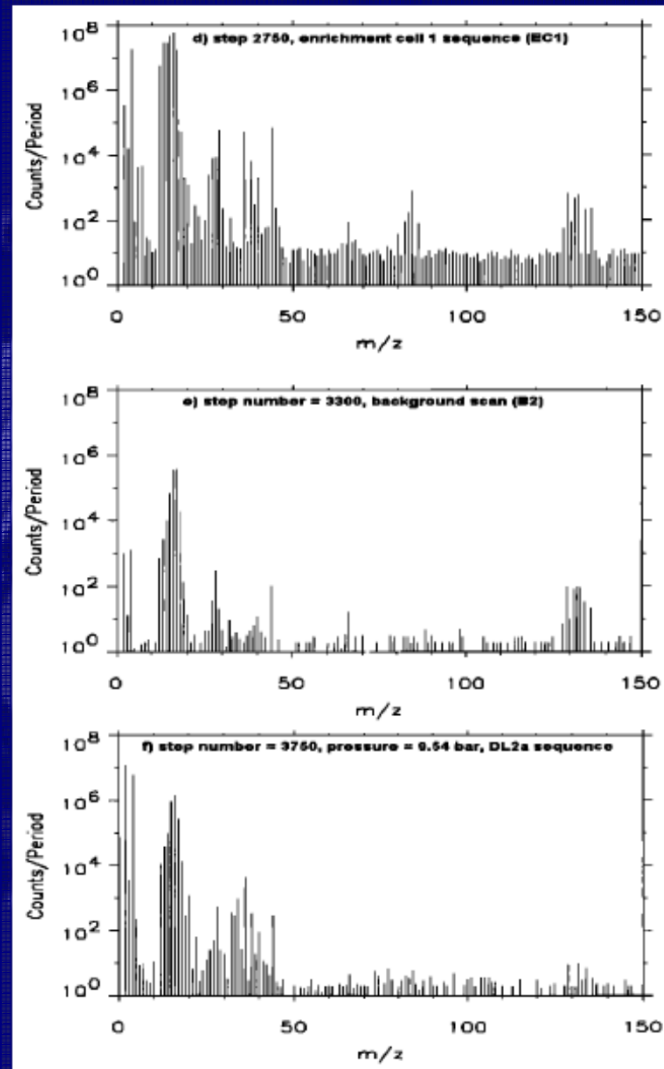


# Exploration of the Jupiter system with the Galileo mission (1995)

## A view of the composition of the upper atmosphere



*Calibration data before and after enrichment*



*Measurements during the descent*



# Exploration of the Jupiter system with the Galileo mission (1995)

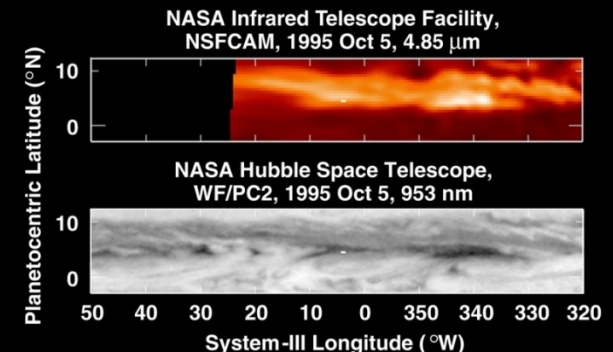
**Table 1.** Measured Mixing Ratios or Isotope Ratios

Species or Ratio	Mixing Ratio $f$ or Isotope Ratio	Mole Fraction $q$	Ratio to Solar
$^4\text{He}$	$0.157 \pm 0.030$	$0.136 \pm 0.026$	0.8
$^3\text{He}/^4\text{He}$	$(1.66 \pm 0.05) \times 10^{-4}$		
D/H	$(2.6 \pm 0.7) \times 10^{-5}$		
$^{20}\text{Ne}$	$\leq 3 \times 10^{-5}$	$\leq 2.6 \times 10^{-5}$	$\leq 0.13$
$^{36}\text{Ar}$	$\leq 10.5 \times 10^{-6}$	$\leq 9.06 \times 10^{-6}$	$\leq 1.7$
$^{84}\text{Kr}$	$\leq 3.7 \times 10^{-9}$	$\leq 3.2 \times 10^{-9}$	$\leq 5$
$^{132}\text{Xe}$	$\leq 4.5 \times 10^{-9}$	$\leq 3.8 \times 10^{-10}$	$\leq 5$
$\text{H}_2\text{O}$			
3.6 bars	$\leq 8 \times 10^{-7}$	$\leq 6.9 \times 10^{-7}$	$\leq 4.1 \times 10^{-4}$
12 bars	$\leq (5.6 \pm 2.5) \times 10^{-5}$	$\leq (4.8 \pm 2.1) \times 10^{-5}$	$\leq 0.033$
19 bars	$\leq (6 \pm 3) \times 10^{-4}$	$\leq (5.2 \pm 2.6) \times 10^{-4}$	$\leq 0.35$
$\text{CH}_4$	$(2.10 \pm 0.4) \times 10^{-3}$	$(1.81 \pm 0.34) \times 10^{-3}$	2.9
$^{13}\text{C}/^{12}\text{C}$	$0.0108 \pm 0.0005$		
$\text{NH}_3$ (>15 bars)	$\leq 2.3 \times 10^{-3}$	$\leq 2 \times 10^{-3}$	$\leq 10$
$\text{H}_2\text{S}$			
3.6 bars	$< 10^{-6}$	$< 8.6 \times 10^{-7}$	$< 0.03$
8.7 bars	$7 \times 10^{-6}$	$6.1 \times 10^{-6}$	0.23
>16 bars	$(7.7 \pm 0.5) \times 10^{-5}$	$6.7 \times 10^{-5}$	2.5
$\text{PH}_3$ (>16 bar)	$\leq 6 \times 10^{-6}$	$\leq 5.2 \times 10^{-6}$	$\leq 8$
Cl	detected		

But measurement not  
representative of the main  
atmospheric component

## Cylindrical Maps of Jupiter: $3^\circ\text{S} - 12^\circ\text{N}$

Extrapolated from 1995 Oct 5 to Dec 7  
Using Eastward Wind Speed = 103 m/s

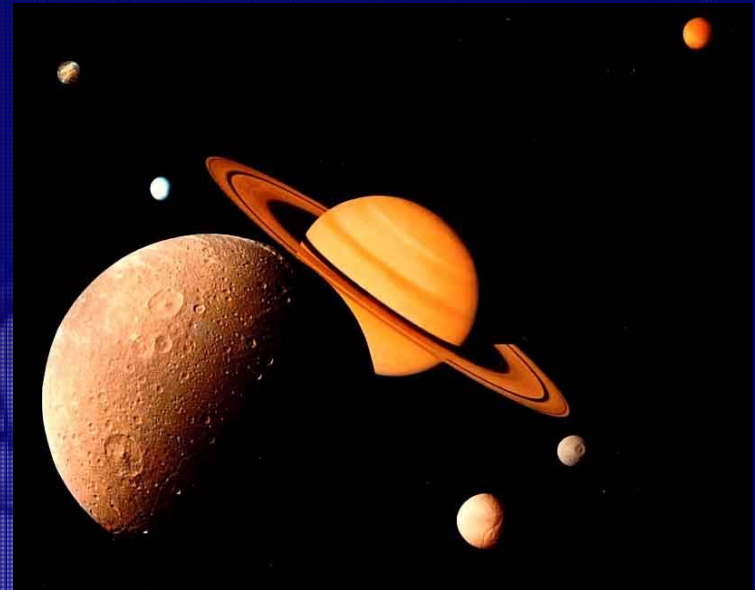




# Exploration of the Saturn system with the Cassini-Huygens mission (2005)

## Interest of Saturn :

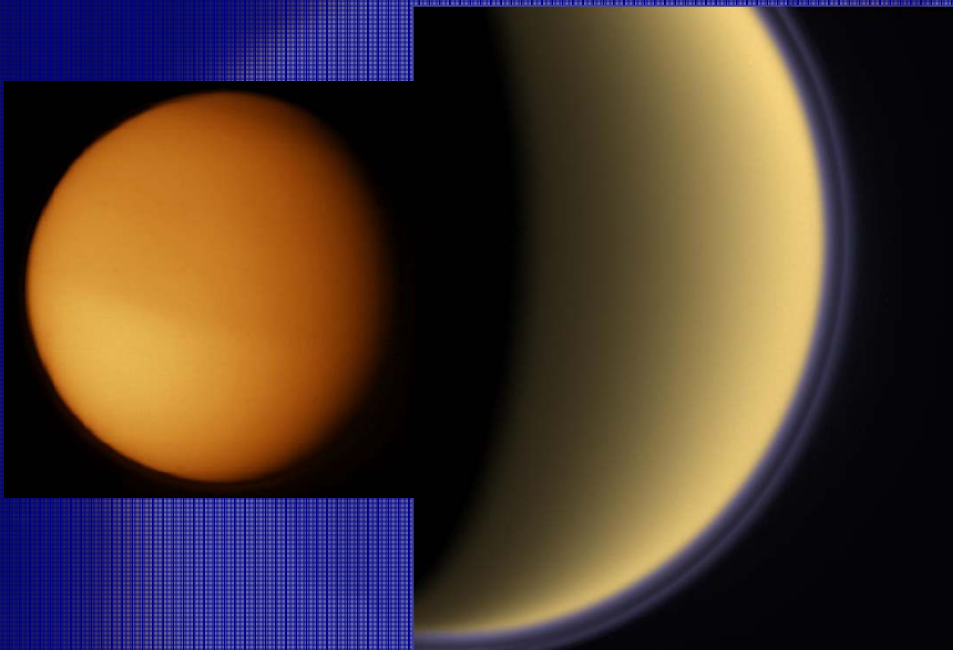
1. Biggest gaseous giant
2. Solar system origin
3. System of satellites
4. System of rings
5. Similarity with exoplanets



*A view of the Saturn system*

## Interest of Titan :

1. Dense atmosphere
2. Organic chemistry
3. Liquid areas at the surface



*Titan as seen by the Voyager and Cassini probes*



# Exploration of the Saturn system with the Cassini-Huygens mission (2005)

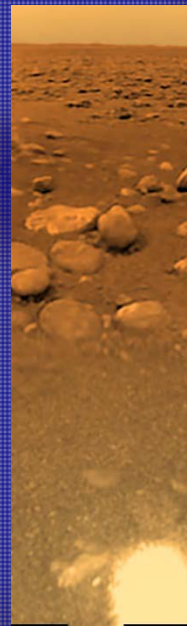
## Cassini Saturn probe :

1. Orbital probe
2. Saturn system exploration
3. Titan fly-bys
4. Saturn environment characterisation

*The Cassini spacecraft in a vacuum chamber*



*Artist view of the Huygens landing*



*Picture of the Titan's surface by the Huygens probe*

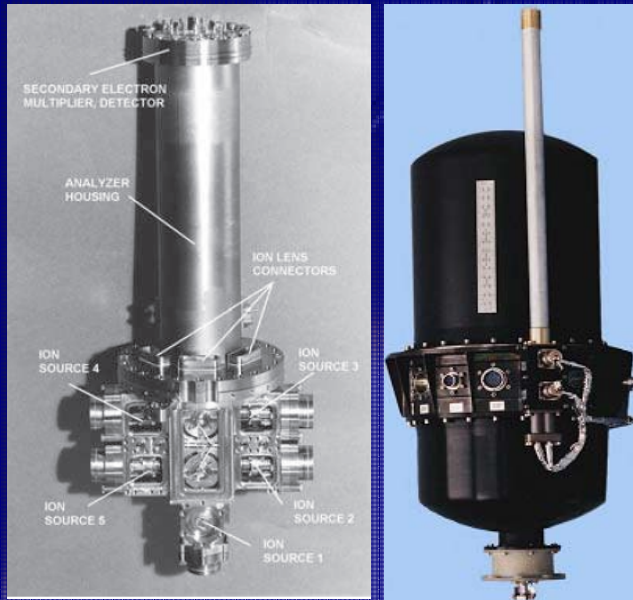
## Huygens Titan probe :

1. Atmospheric probe
2. Atmospheric properties
3. Surface characterisation



# The Cassini-Huygens mission (2005) Unveiling Titan

## The GCMS experiment onboard the Huygens probe :



*The GCMS experiment and its quadrupolar filter*

Couple with the Aerosol Collector and Pyrolyzer experiment for the analysis of the aerosols composition

## MS main specifications :

Nature : Quadrupole

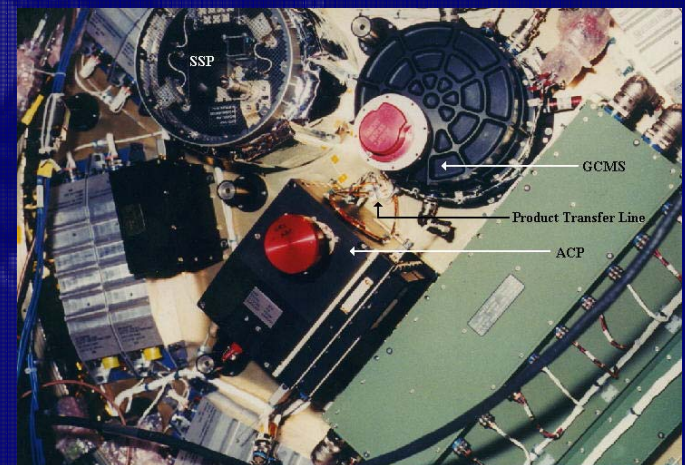
Mass : ~17 kg

Volume : ~20 cm  $\varnothing$  x 47 cm H

Power : 41 W

m/z range : 2-141

Sensitivity : ~10 ppbv

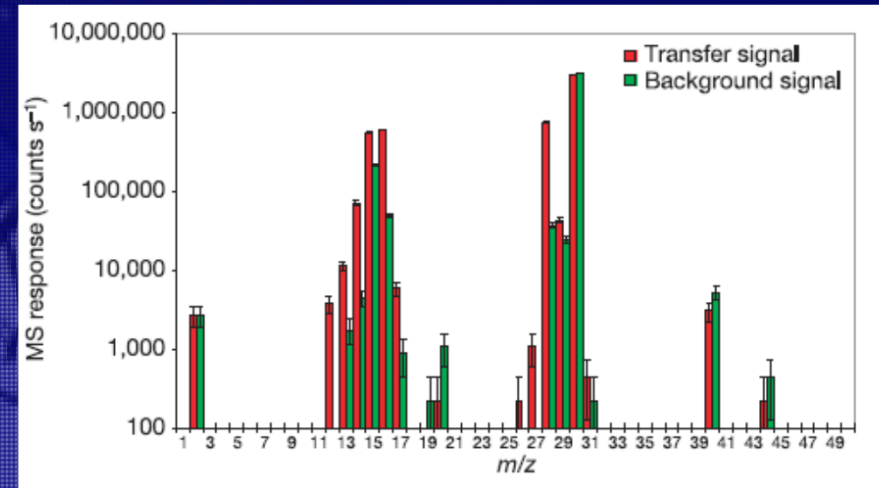
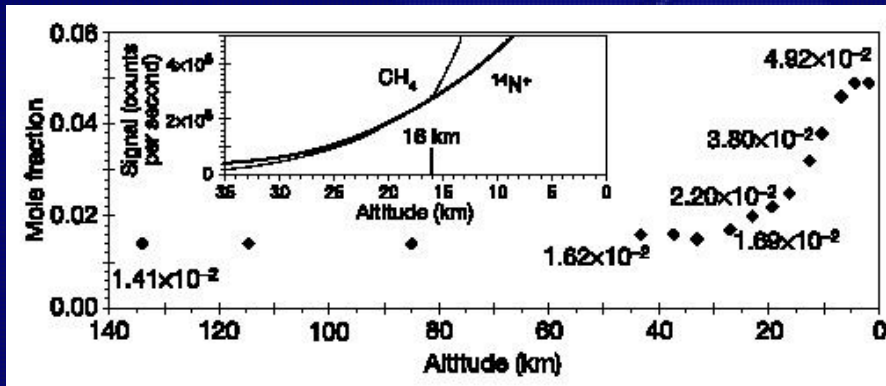


*The GCMS experiment coupled with the ACP experiment in the Huygens probe*

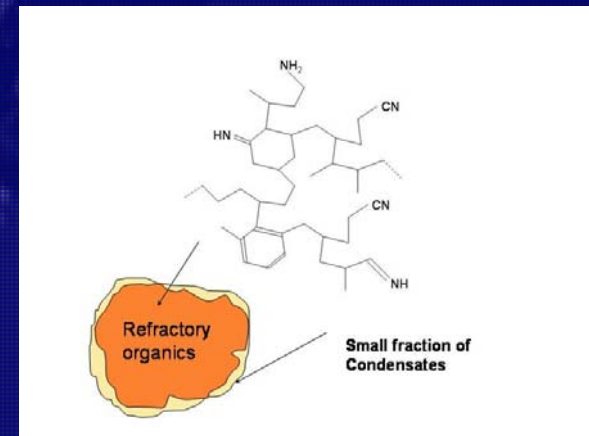
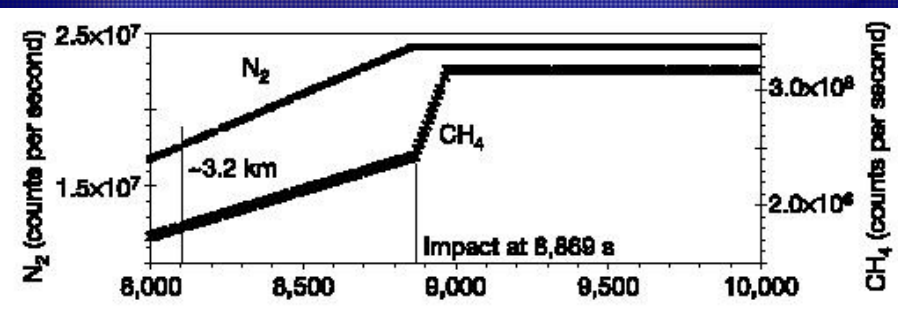
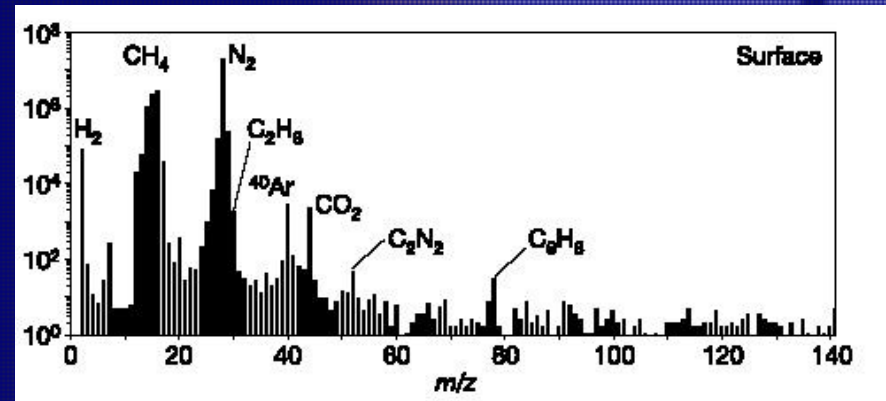


# The Cassini-Huygens mission (2005) Unveiling Titan

A new idea of the Huygens atmosphere and surface :



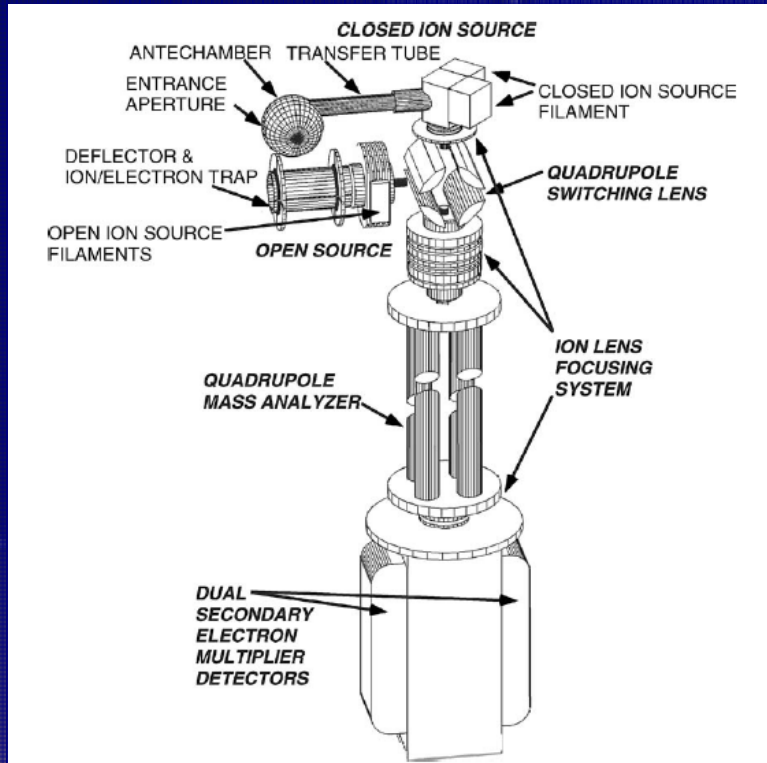
*Aerosols pyrolysates (from ACP) analysis*





# The Cassini-Huygens mission (2005) : What is there in the Saturn suburbs ?

## The INMS experiment onboard the Cassini probe :



*INMS experiment schemes*

## MS main specifications :

Nature : Quadrupole

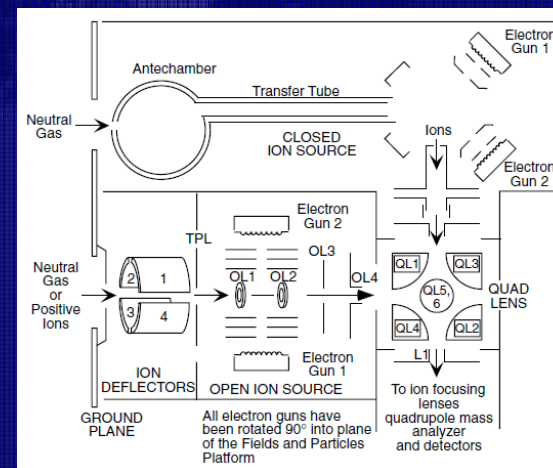
Mass : ~11 kg

Volume : ~30 L

Power : 23 W

m/z range : 1-99

Sensitivity : N/A

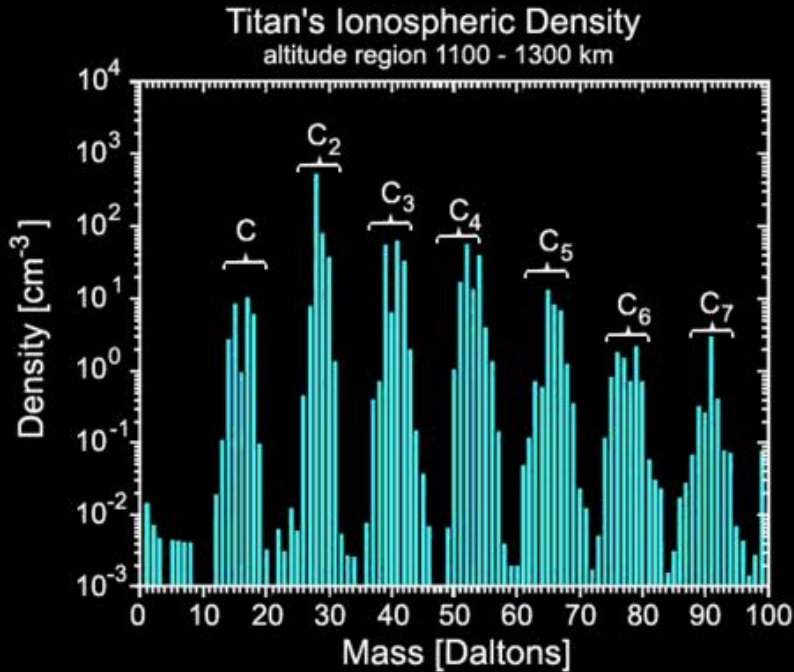




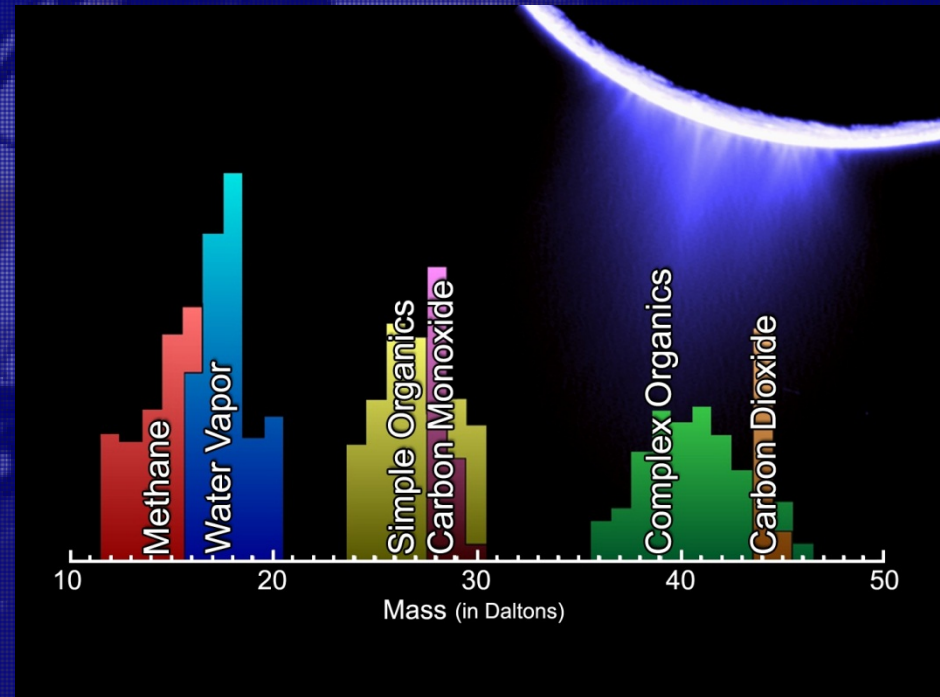
# The Cassini-Huygens mission (2005)

## What is there in the Saturn suburbs ?

My system is rich !



*INMS analysis done in the Titan upper atmosphere*



*INMS analysis done in the Enceladus plumes*



# Return to Mars : The Phoenix Mars polar probe and the search for water and minerals (2007)

## Phoenix probe & objectives :

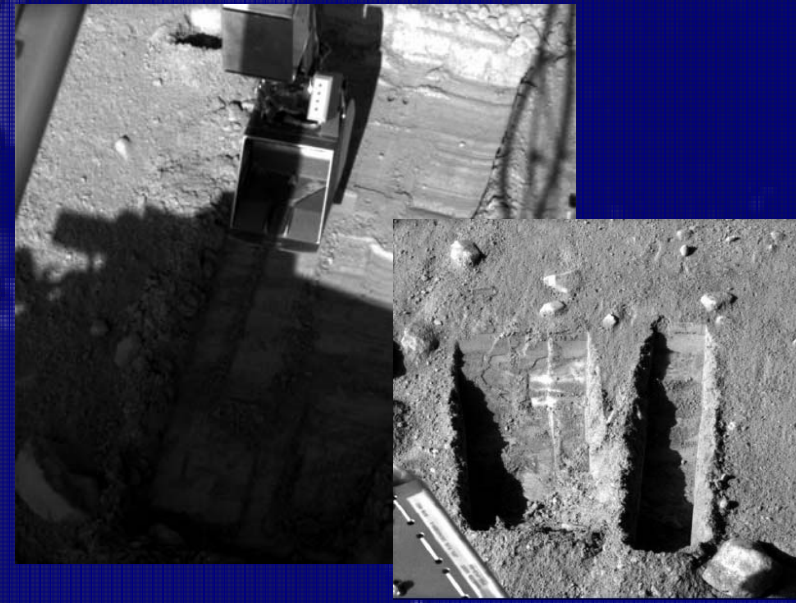
1. Lander ( )
2. Water at the pole
3. Mineralogy
4. Environment



*Artist view of Phoenix*



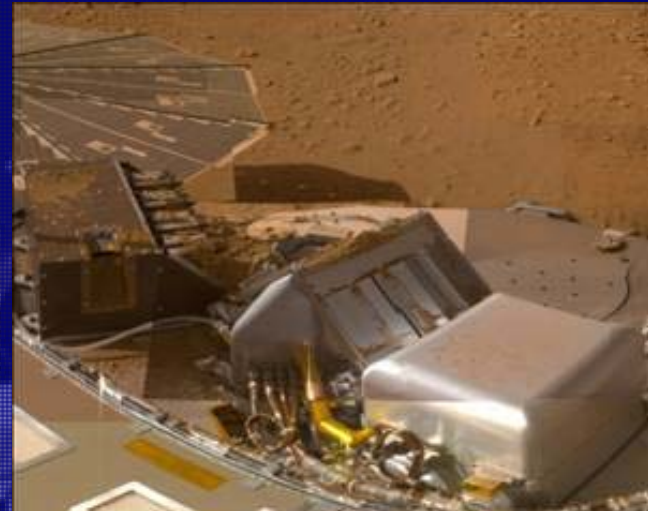
*Pictures of Phoenix on Mars*



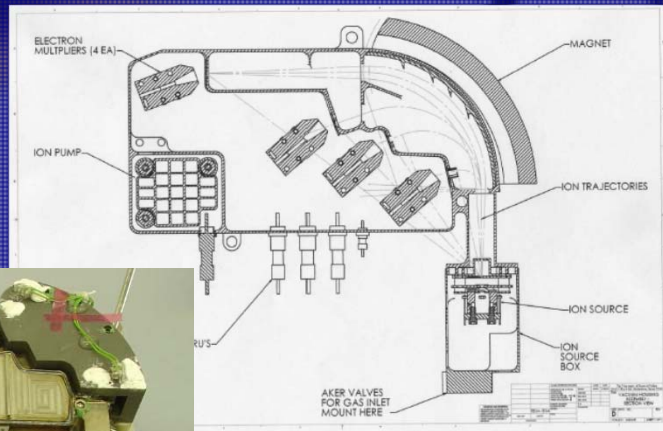


# The Phoenix mission and the search for water and mineralogy

The TEGA experiment to analyse the atmosphere and the content of the soil (calorimeter+evolved gas analyzer)



*Picture of TEGA on Phoenix*



*Picture and scheme of the TEGA mass spectrometer*

## MS main specifications :

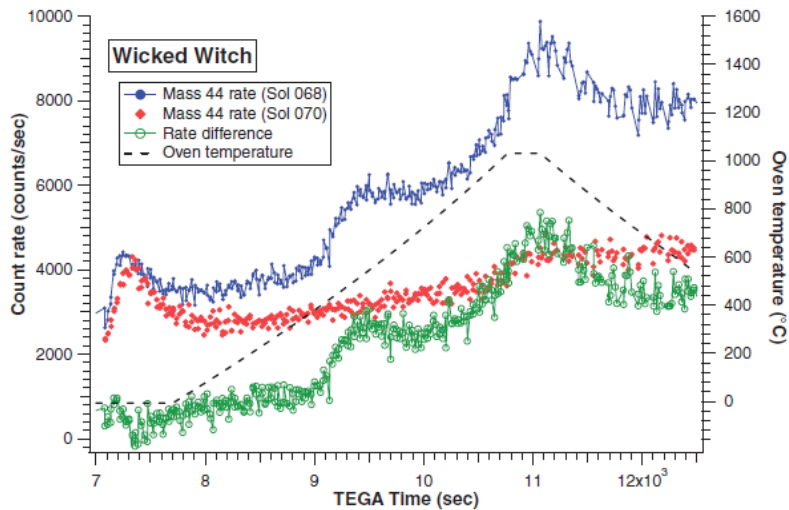
Nature :	Sector (B)
Mass :	~6 kg
Volume :	~20 cm <sup>3</sup>
Power :	13 W
m/z range :	1-140
Sensitivity :	10-100 ppbv





# The Phoenix mission and the search for water and mineralogy

## TEGA found $\text{CO}_2$ in the atmosphere and limestone in the soil

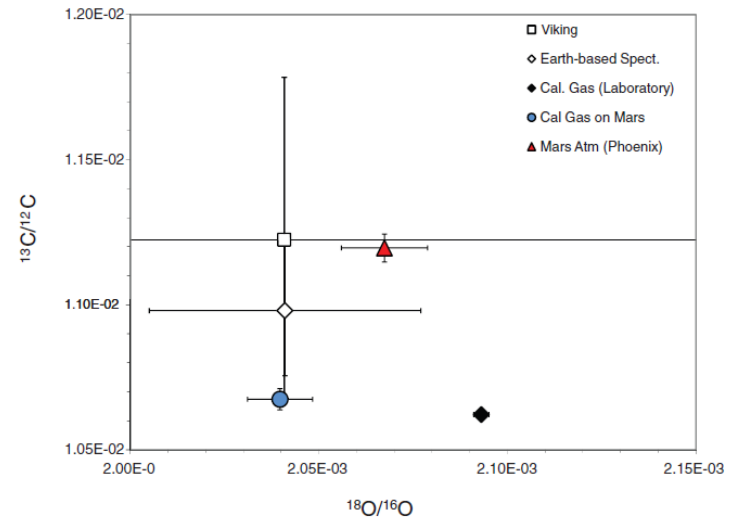
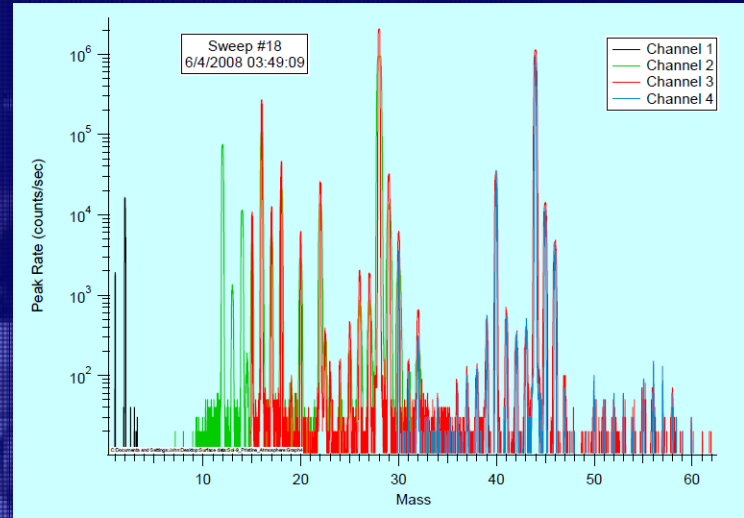


**Fig. 2.** Plot of Mass 44 ( $\text{CO}_2$ ) count rate and temperature versus run time. The first peak is atmospheric  $\text{CO}_2$  that diffuses into the oven and plumbing overnight; the second may be due to carbonates with a low decomposition temperature (e.g.,  $\text{FeCO}_3$  or  $\text{MgCO}_3$ ). The high temperature peak is due to decomposition of  $\text{CaCO}_3$ .

*Detection of carbonates by following the  $\text{CO}_2$  outgassing during the pyrolysis (Boynton et al., 2009)*

*A new measurement of the  $\text{CO}_2$  isotopic ratios in the atmosphere*

*(Niles et al., 2010)*

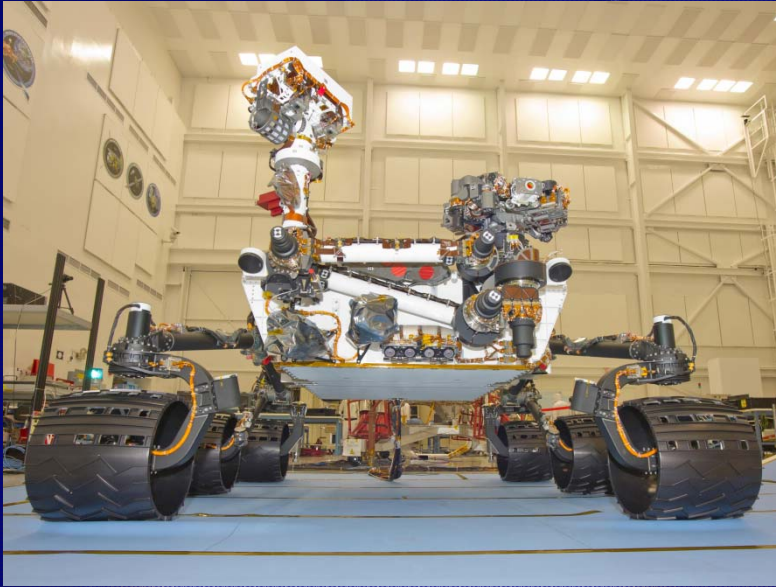


**Fig. 2.** Corrected and calibrated results of martian atmospheric  $\text{CO}_2$  measurement plotted next to results from Viking lander (28, 29), Earth-based spectroscopy (2), and measurements of calibration gas on Earth and Mars. The result for calibration gas on Mars is the uncalibrated value to show the magnitude of the calibration correction. Error bars on TEGA measurements are  $2\sigma$  SE.



# Assessing the Mars habitability with the Mars Science Laboratory mission (2012 NOW !!)

## Curiosity : a monster rover in an ancient wet crater



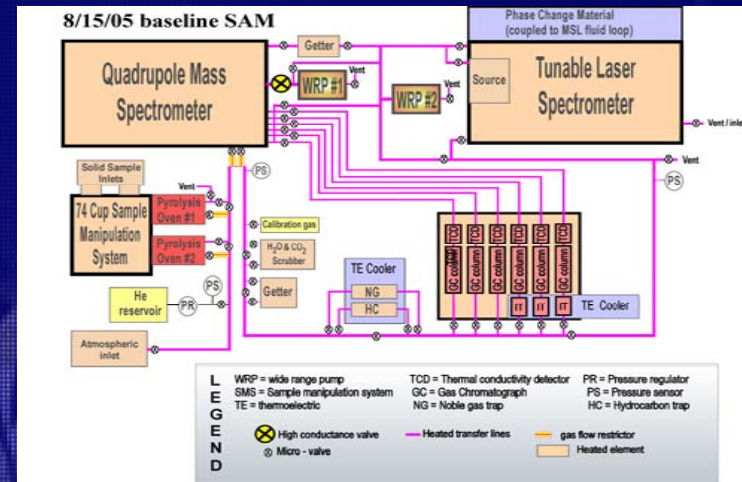
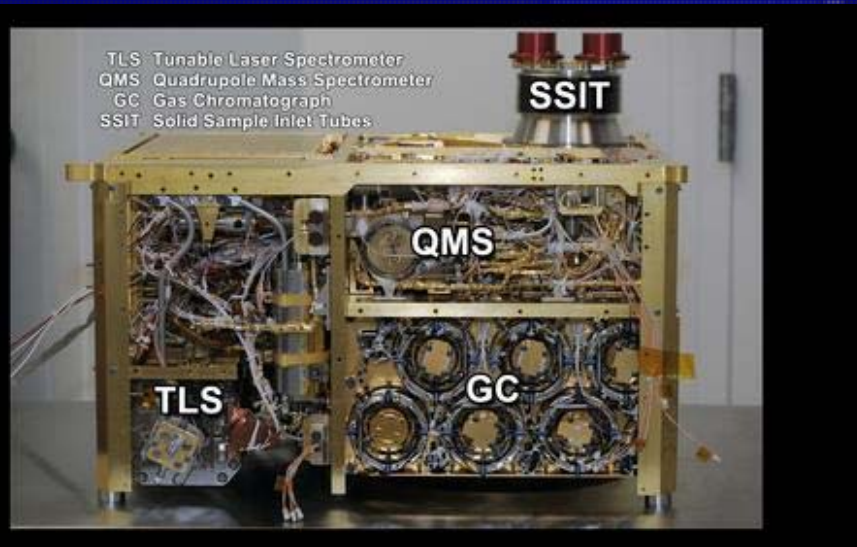


# The Mars Science Laboratory mission (2012 NOW !!)

## The Sample Analysis at Mars (SAM) experiment or the

### Curiosity “swiss knife” :

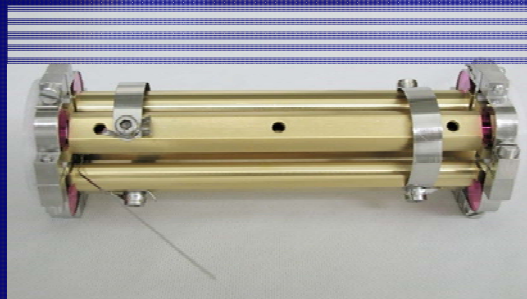
1. Atmosphere (CH<sub>4</sub>)
2. Mineralogy (EGA)
3. Organics in the soil



Principle scheme of SAM (Mahaffy et al., in press)

## SAM main specifications :

- Nature : Quadrupole
- Mass : ~30 kg
- Volume : ~45 L
- Power : 50 W
- m/z range : 2-450
- Sensitivity : 1 ppbv

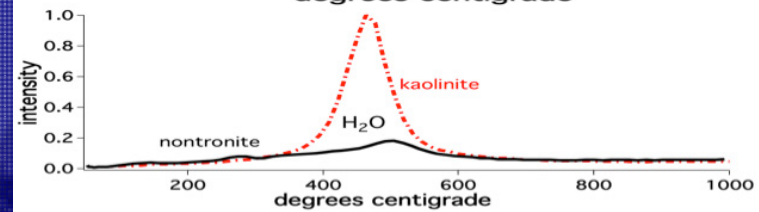
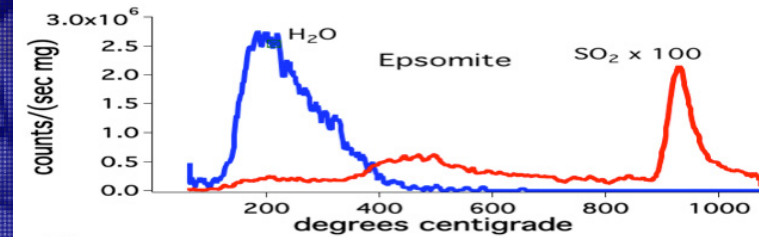
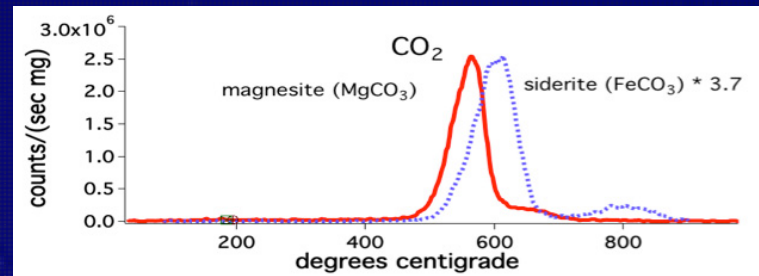
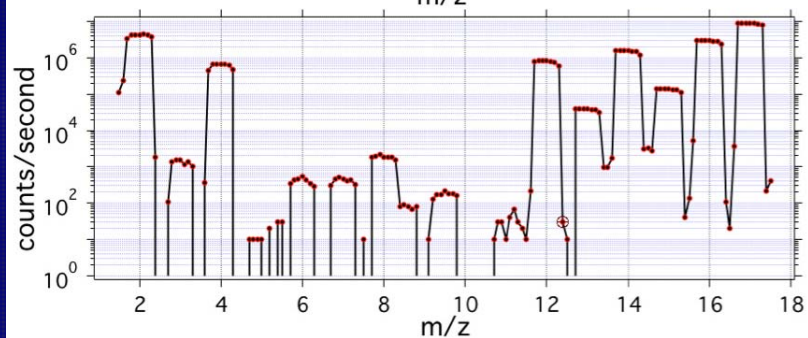
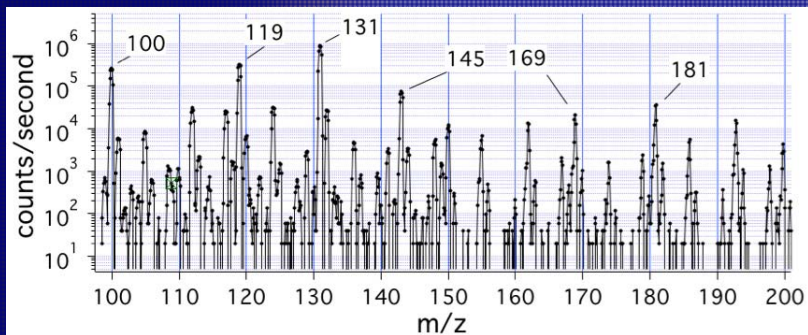
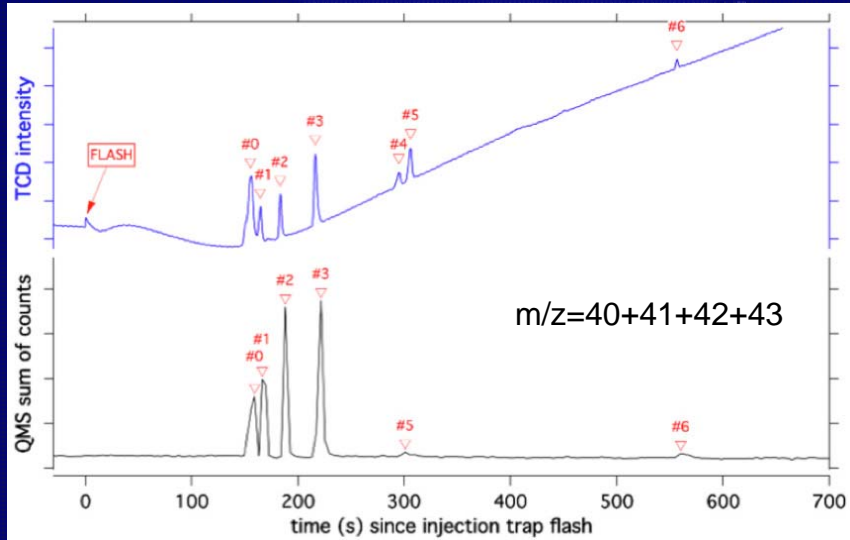


Pictures of SAM and the quadrupolar filter



# The Mars Science Laboratory mission (2012 NOW !!)

## How SAM will assess the Mars habitability ?

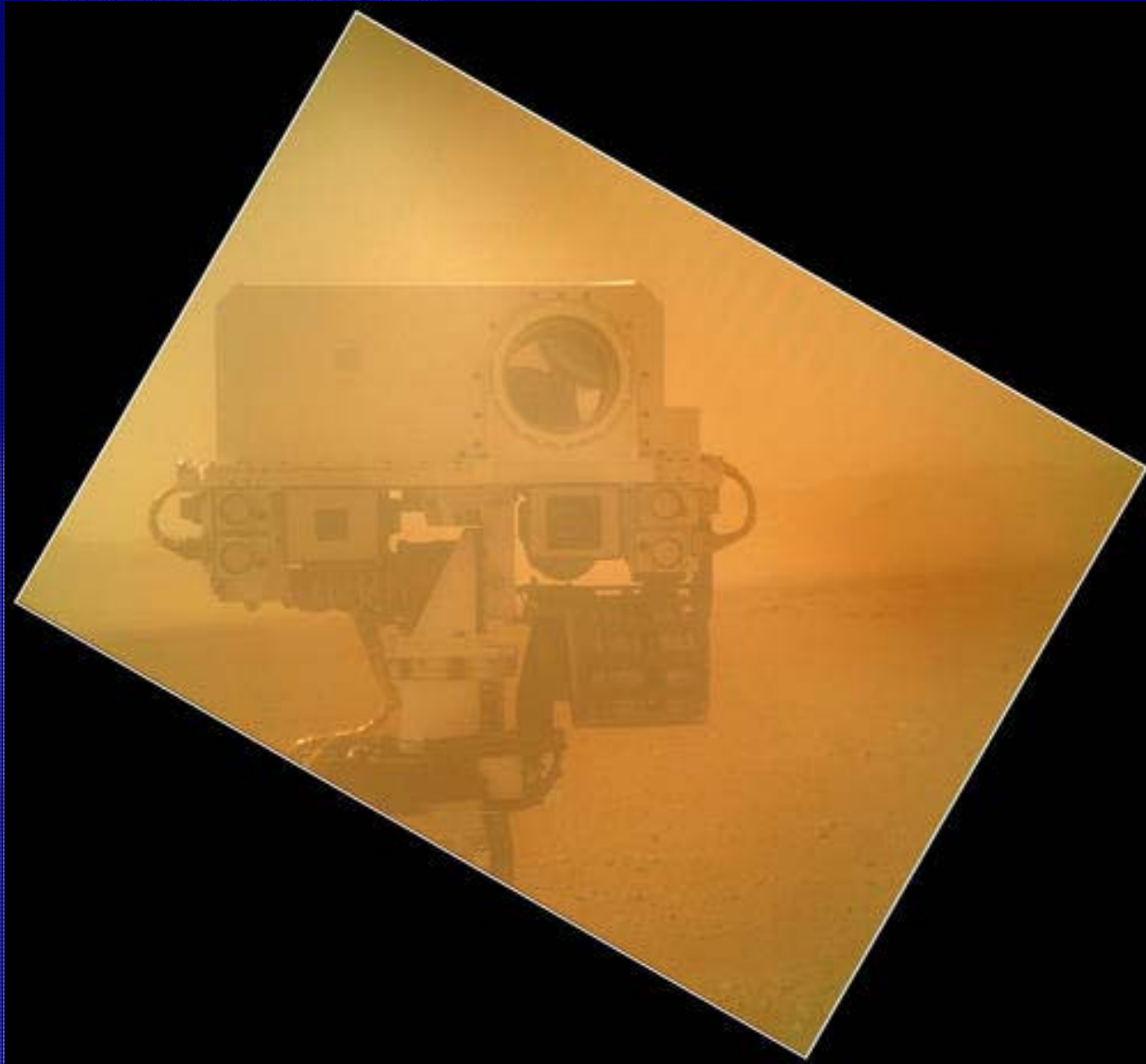


*Mineralogical measurements (Mahaffy et al., in press)*

*Look for organics in the atmosphere and in the soil  
(Mahaffy et al., in press)*



# AND TOMORROW ?





# The Rosetta mission to a comet (2014): Tomorrow is today !

## Objectives :

1. Properties of a cometary nucleus
2. Evolution of the cometary environment with time



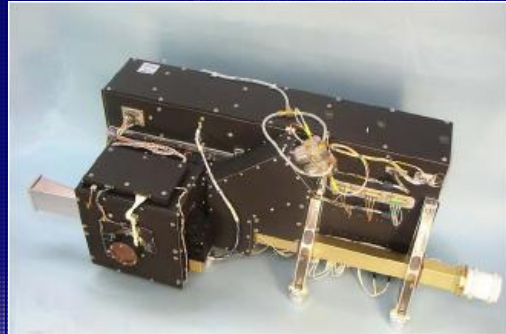


# Mass spectrometry in Rosetta

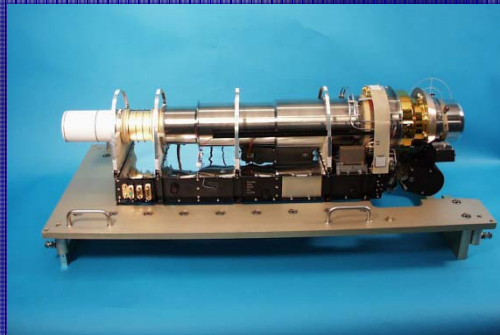
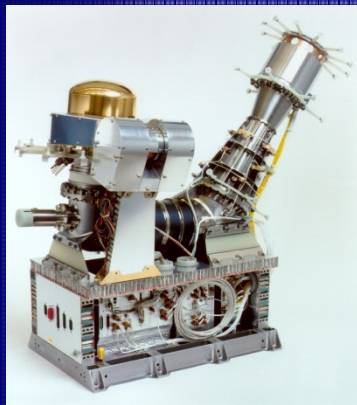
## 4 experiments based on mass spectrometry

### 2 in the orbiter

**COSIMA** : composition of dust grains in the coma



**ROSINA** : composition of neutral and ion species in the coma



### 2 in Philae

**MODULUS** : isotopic composition of the nucleus solid material



**COSAC** : molecular composition of the nucleus solid material



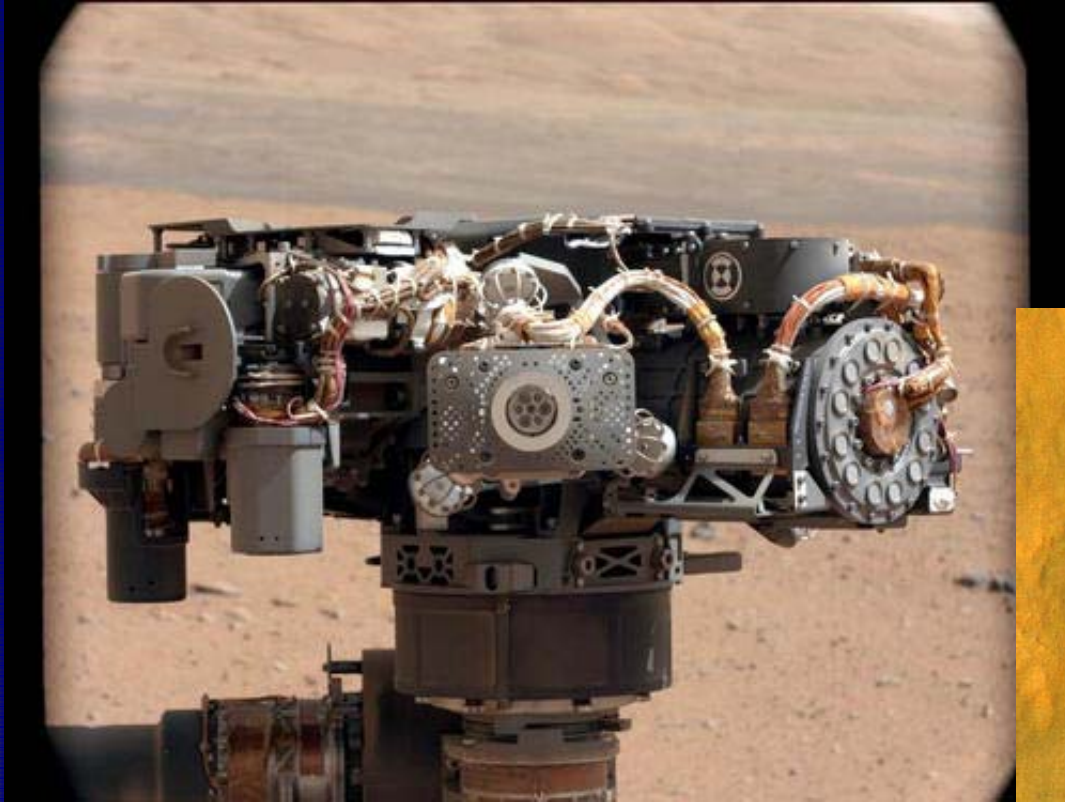


# Mass spectrometry in Rosetta

MS name	Sample nature	MS Type	Mass (kg) Size (mm)	Power (W)	m/z range	Resolution
COSIMA	Grains in the coma	TOF		20	1-1300	2000 / 50%
ROSINA	Gas in the coma	DFMS	16.2 630×630×260	19	12-150	3000 / 1%
		TOF	14.7 1140×380×240	24	1-350	>500 / 1%
COSAC	Nucleus surface material	TOF	1.5 460×80×80	15	1-1500	350 / 50%
PTOLEMY	Nucleus surface material	IT	0.5 80×100×55	10	12-150	

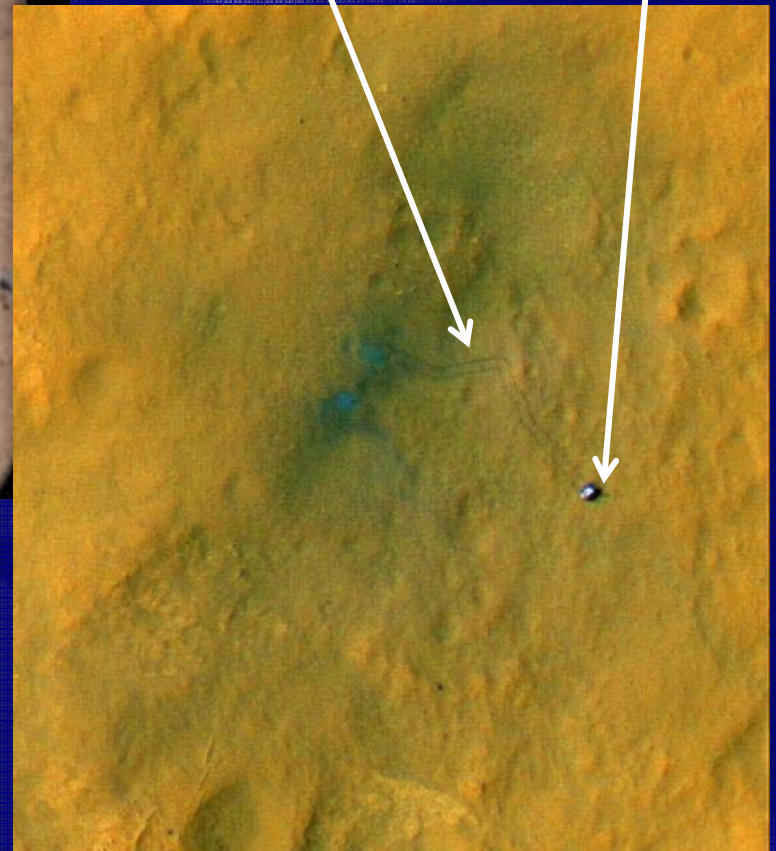


# AND THE DAYS AFTER ?



*Traces des roues*

*Curiosity*





# How can we improve MS for space exploration ?

## 1. MS resolution :

Very high resolution to help the species identification

↳ Orbitrap or FTICR in space ?



*Orbitrap core*

## 2. Improve the vacuum :

More efficient pumping systems (HRMS, hyphenated techniques...)

## 3. Ionisation sources :

Less resources (mass, power) consuming sources

↳ nanotips ion sources... ?



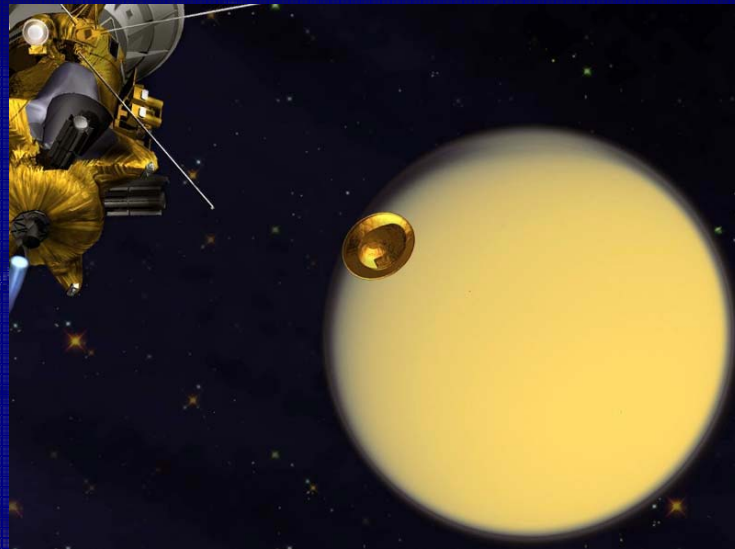
*Ion source of the Ptolemy experiment*

## 4. Sensitivity :

Improve the sensitivity

↳ Integration processes, detectors... ?





THANK YOU



РОСКОСМОС

ФЕДЕРАЛЬНОЕ КОСМИЧЕСКОЕ АГЕНТСТВО  
ФГУП "НПО им. С.А. Лавочкина"  
РОССИЙСКАЯ АКАДЕМИЯ НАУК  
ИКИ РАН

ИКИ РАН

МЕЖДУНАРОДНЫЙ ПРОЕКТ  
«ФОБОС-ГРУНТ»



A satellite with two large blue solar panel arrays is shown in space. The Earth is visible in the background, partially obscured by a bright, glowing atmospheric layer. The word "BACKUP" is overlaid in red, bold, sans-serif font in the center of the image.

**BACKUP**



# ROSINA

## Rosetta Orbiter Spectrometer for Ion and Neutral Analysis

**Principal Investigator** : H. Balsiger, Univ. Bern, Sw.

**Objectives** : determine, the elemental, isotopic and molecular composition of the coma

**Samples** : neutral and ionized gases present in the coma

**Method** : Double Focusing Mass Spectrometer (DFMS) and Time of Flight (TOF)

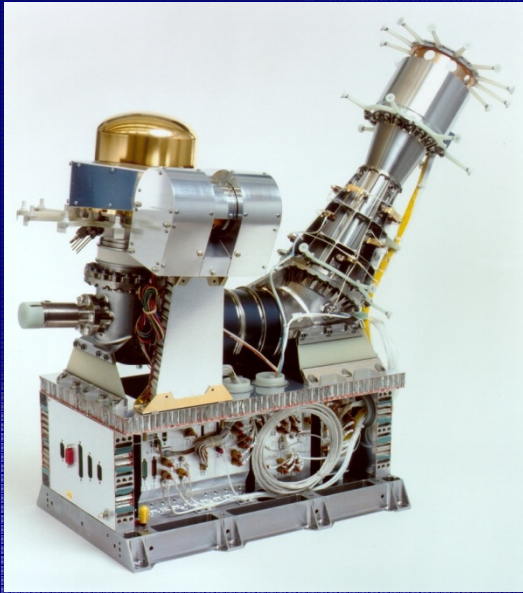
**Location** : in the Rosetta orbiter



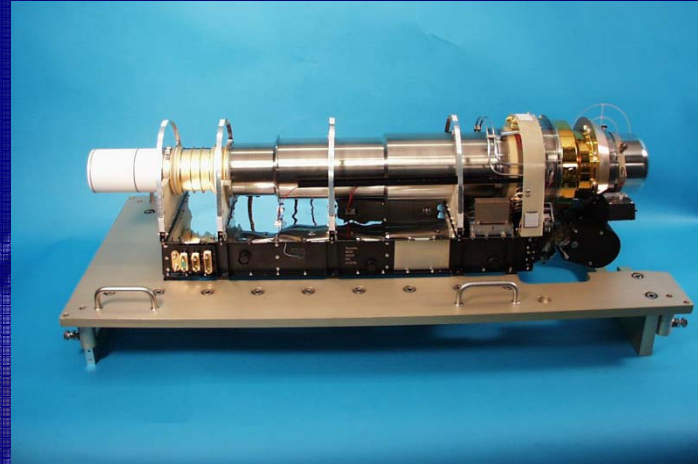
# ROSINA

## General description

3 instruments in 1 experiment : DFMS (double focusing magnetic mass spectrometer), RTOF (reflectron TOF), COPS (pressure sensor)

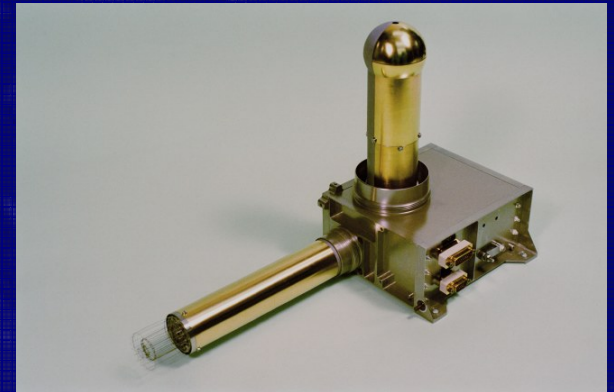


**DFMS**



**RTOF**

**COPS**



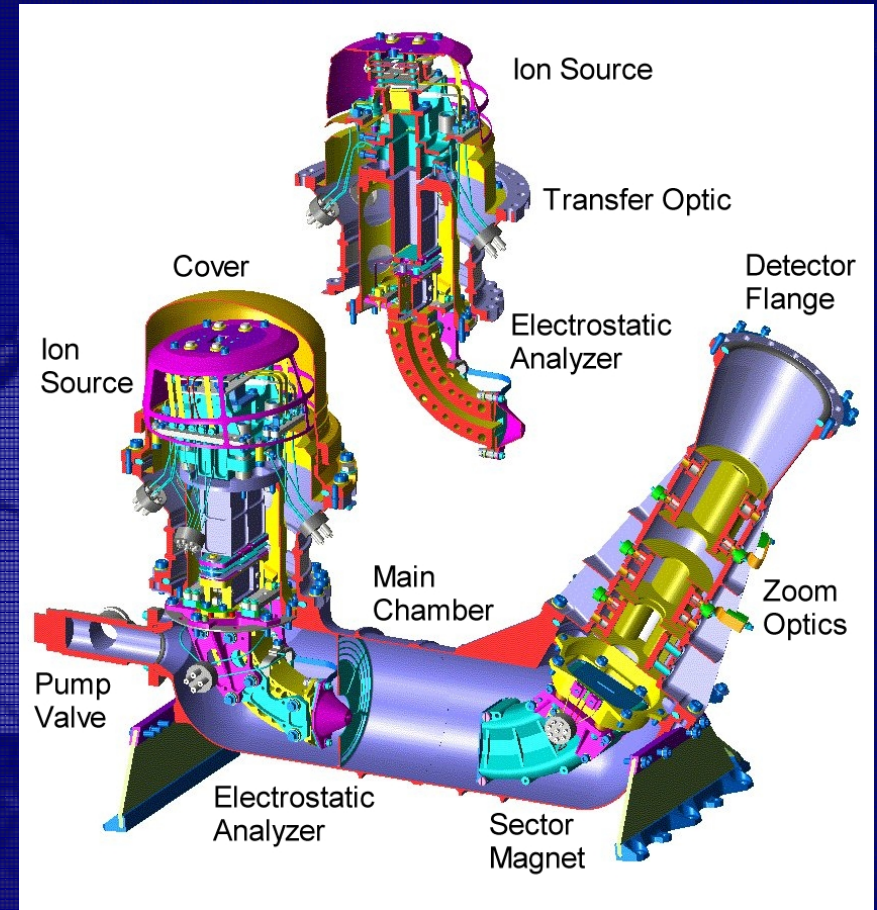
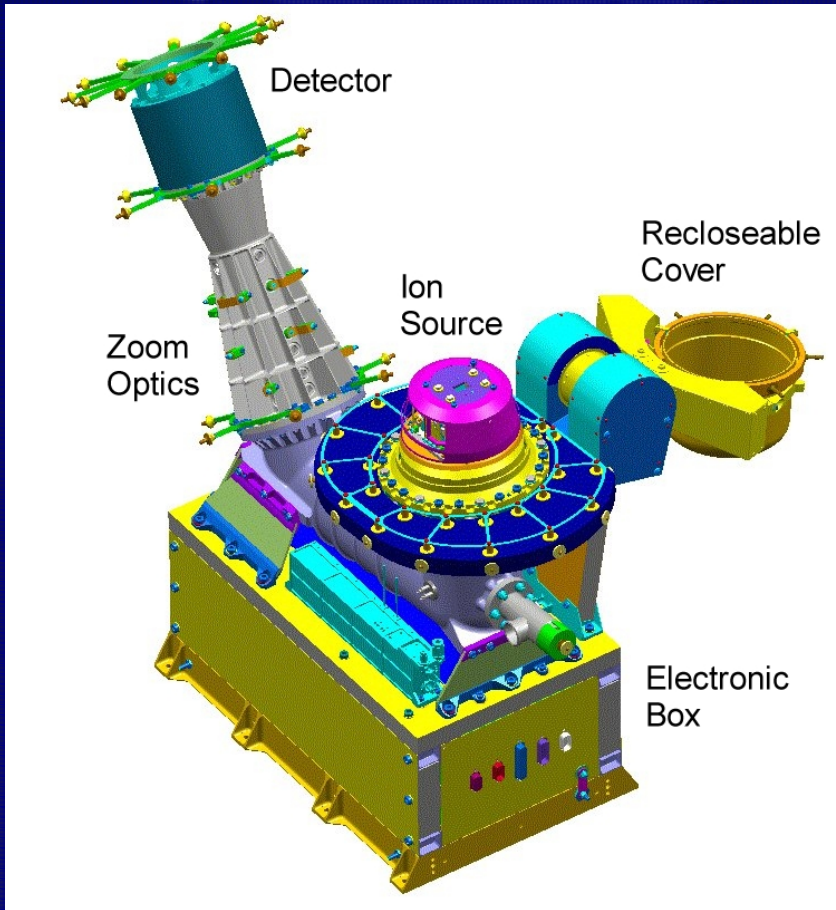
### Instrument characteristics :

**Mass=34.8 kg**

**Mean power consumption : 49 W**



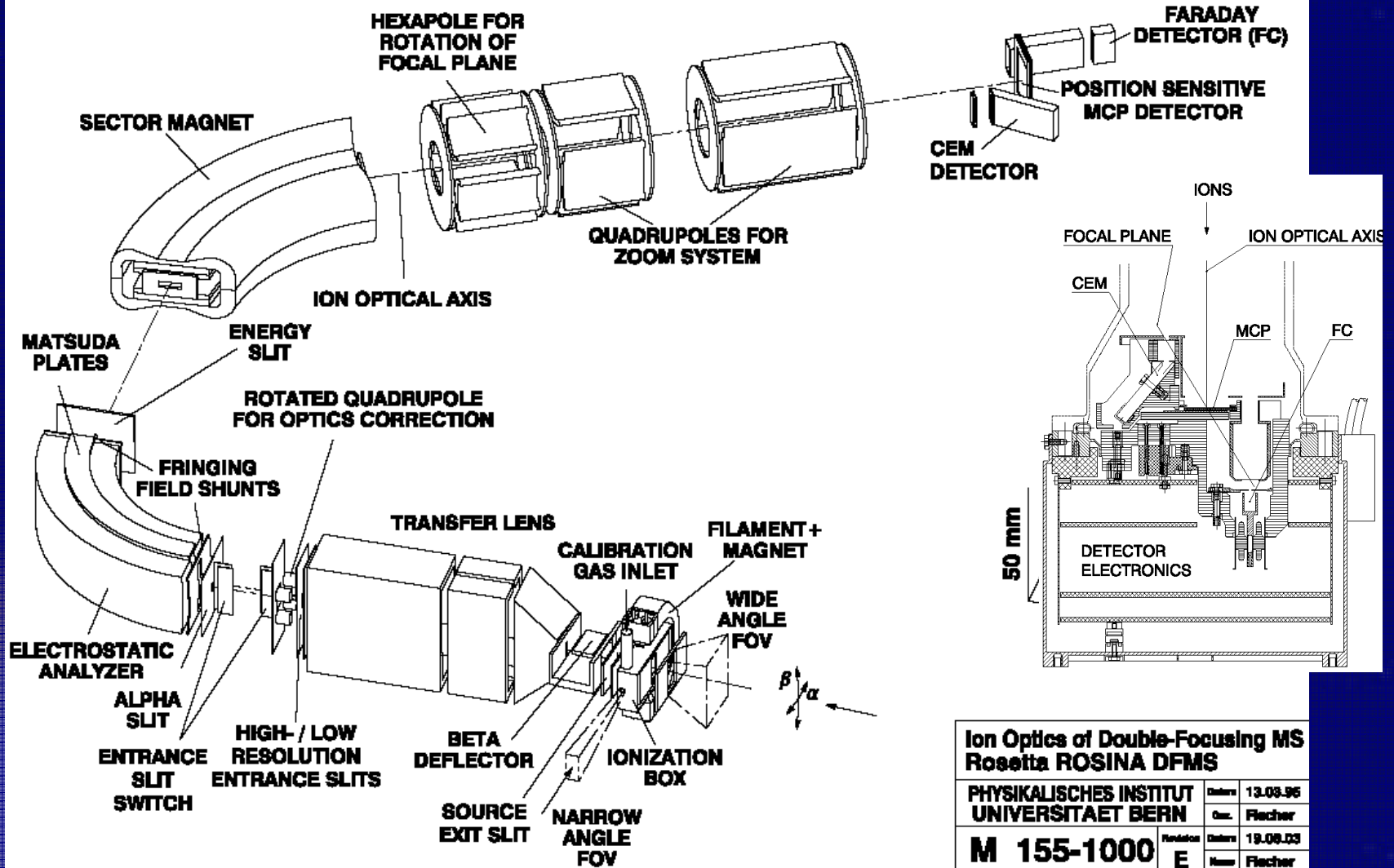
# ROSINA Mass spectrometers DFMS



- Mattauch-Herzog design
- Ions and neutral gas analyzer (2 modes)
- Ion source=e- provided by thermal effect and generated with filaments ( $E(e^-)=10-90$  eV)



# ROSINA Mass spectrometers DFMS



**Ion Optics of Double-Focusing MS  
Rosetta ROSINA DFMS**

PHYSIKALISCHES INSTITUT UNIVERSITÄT BERN	Order	13.08.95
	Doc.	Flecher
<b>M 155-1000</b>	Revision	18.08.03
	Rev.	Flecher



# ROSINA Mass spectrometers

## DFMS

### Mass spectrometers characteristics :

Type : DFMS

Dimensions : 630×630×260 mm/Mass : 16.2 kg

Range : 12-150 Da

Resolution :  $m/\Delta m=3000$  @ 1%

Power consumption : 19 W

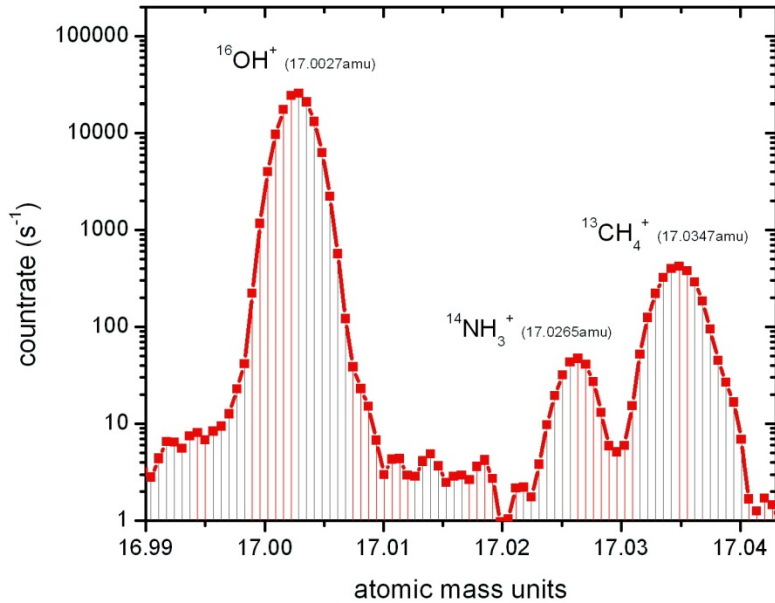
Source=e- provided by thermal effect and generated with filaments ( $E(e^-)=10-90$  eV)

Detector=Microchannel plates (MCPs)+Channel Electron Multiplier (CEM)+Faraday Cup (FC)

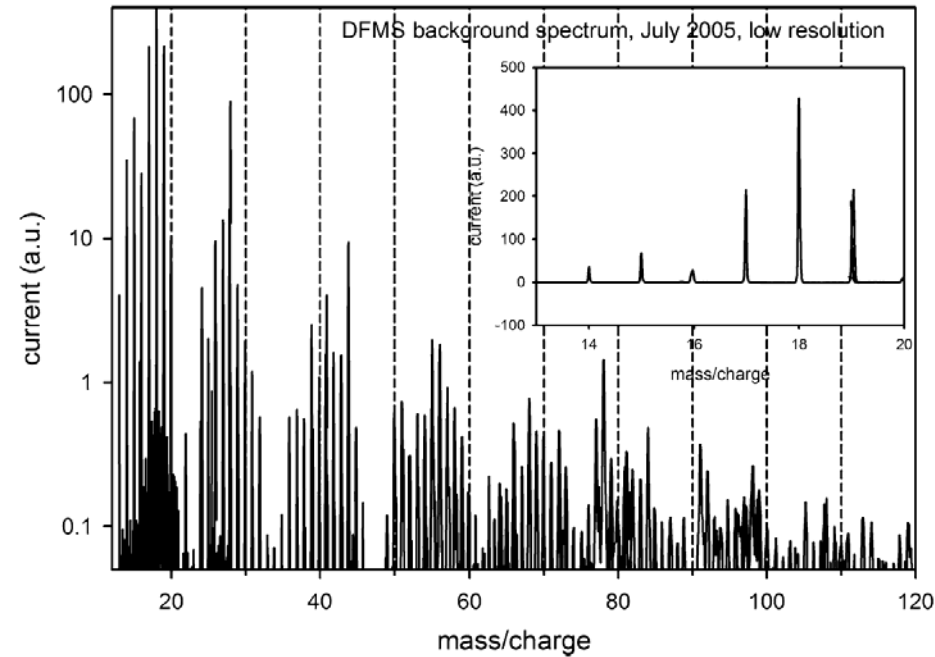


# ROSINA Mass spectrometers

## DFMS



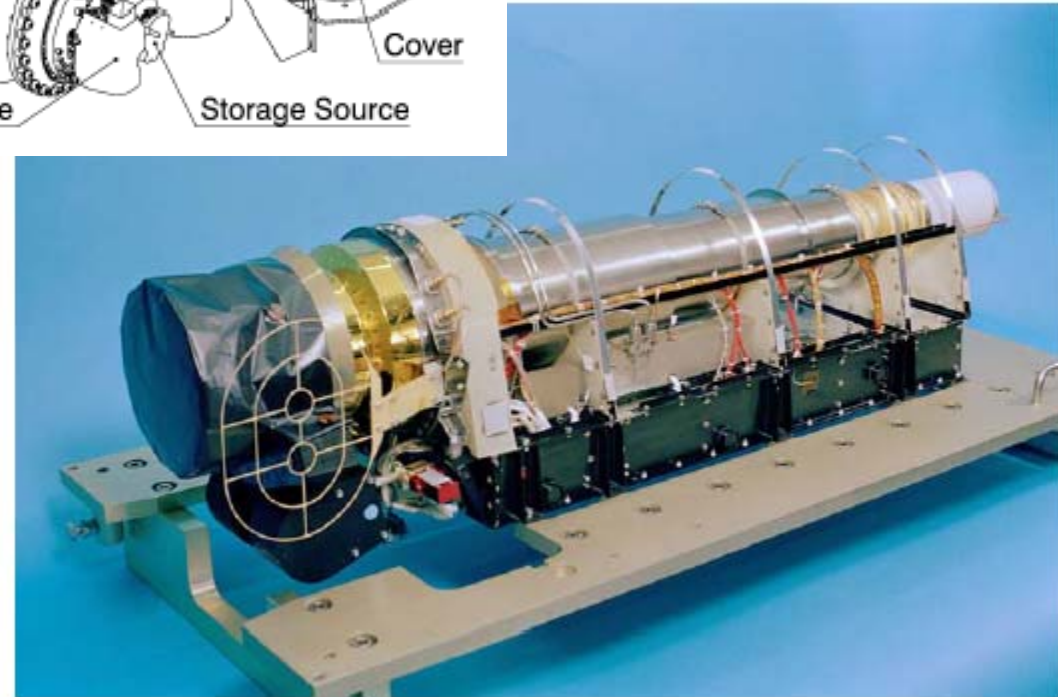
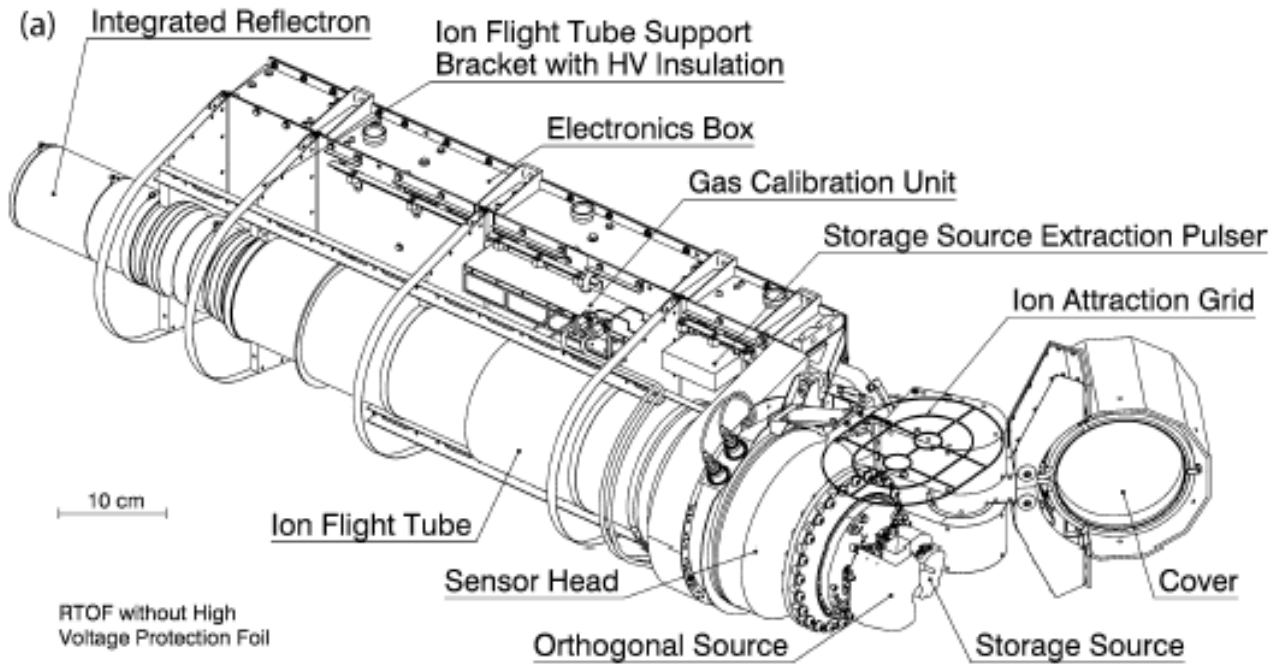
Example of HR mass spectrum recorded with DFMS at the lab



Example of LR mass spectrum recorded in flight with DFMS

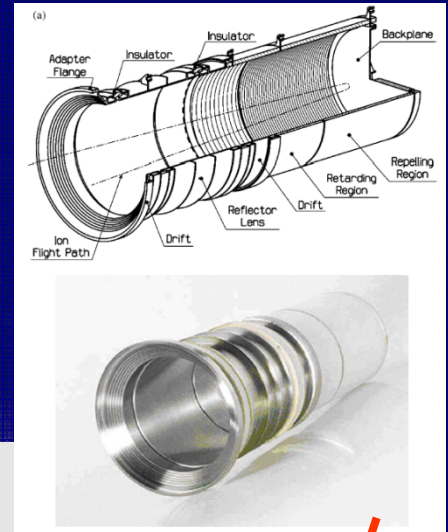
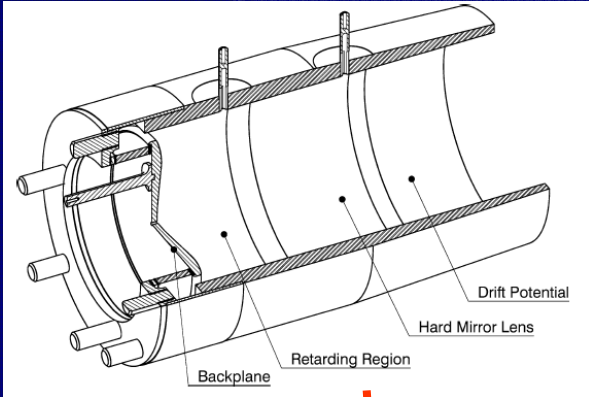


# ROSINA Mass spectrometers RTOF

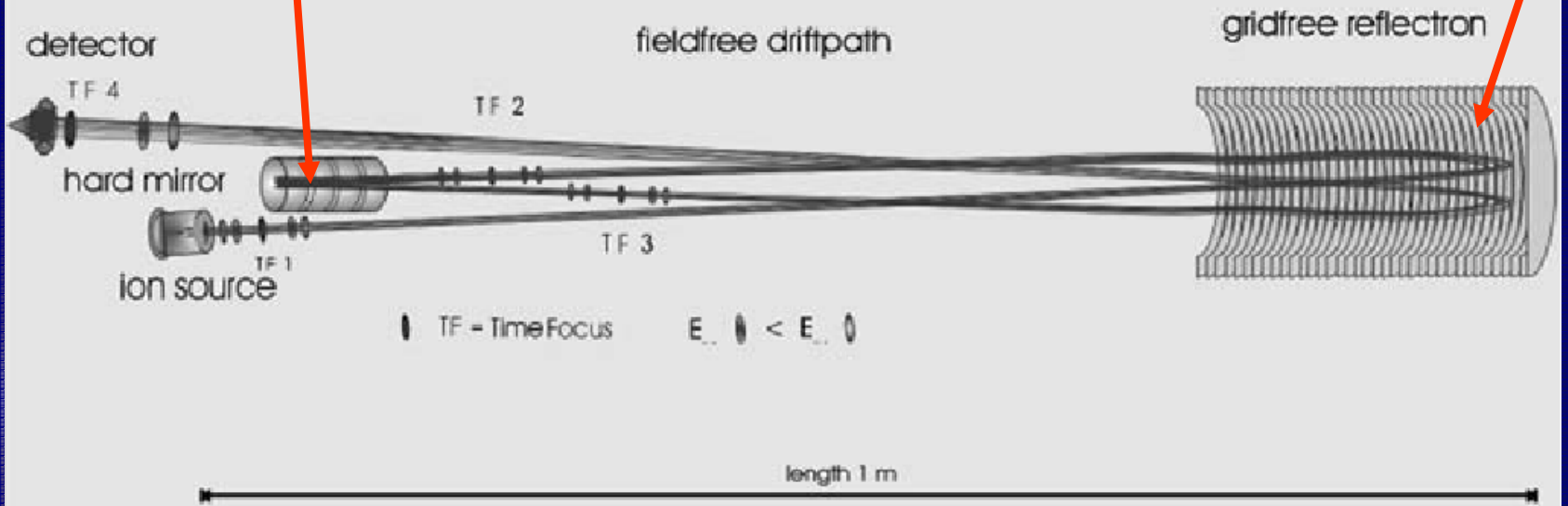




# ROSINA Mass spectrometers RTOF



## ROSINA/RTOF principle scheme





# ROSINA Mass spectrometers RTOF

## Mass spectrometers characteristics :

Type : Reflectron Time of Flight (RTOF)

Dimensions : 1140×380×240 mm/Mass : 14.7 kg

Range : 1-→350 Da

Resolution :  $m/\Delta m > 500$  @ 1%

Power consumption : 24 W

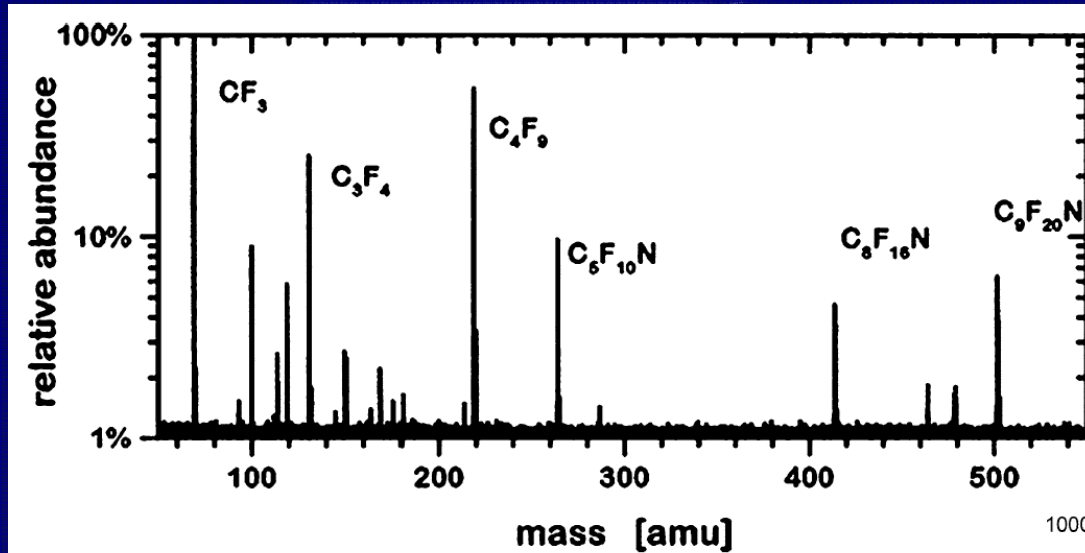
Source=e- from a heated filament of 70 eV energy or  
more

Detector=Microchannel plates (MCPs)

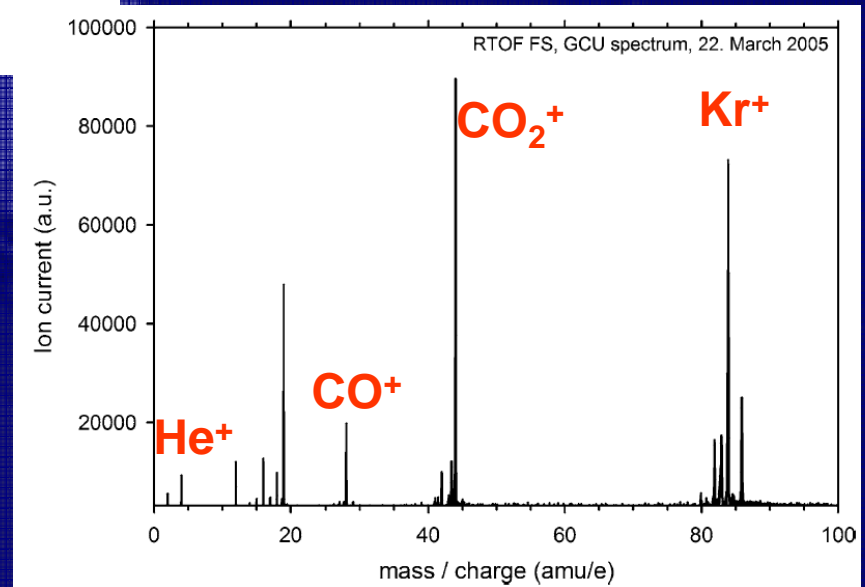


# ROSINA Mass spectrometers

## RTOF



Example of mass spectrum recorded with  $(\text{CF}_3(\text{CF}_2)_3)_3\text{N}$  at the lab

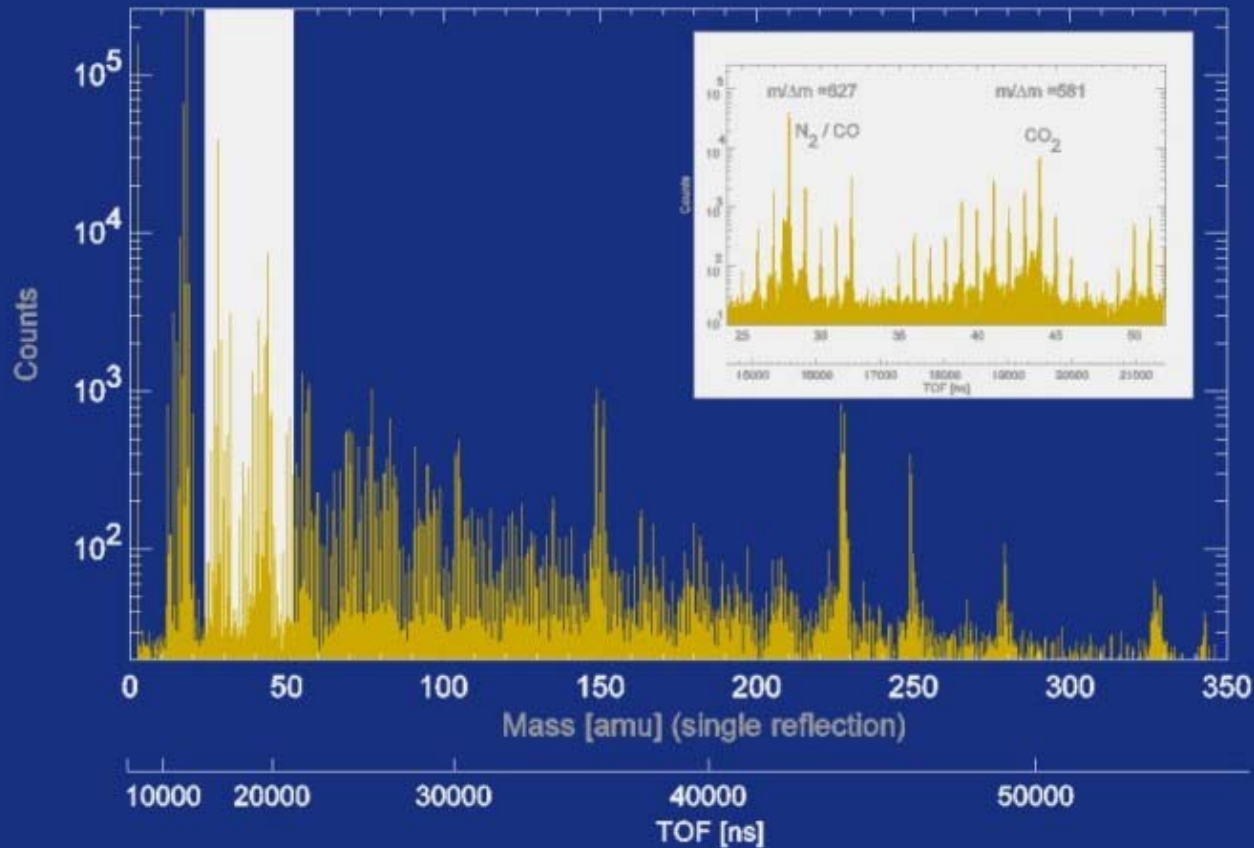


Example of mass spectrum recorded in flight with the calibration gas



# ROSINA Mass spectrometers RTOF

## RTOF Calibrations spectrum of residual gas in vacuum chamber



Example of HR mass spectrum recorded in lab



# COSIMA

## COMetary Secondary Ion Mass Analyzer

**Principal Investigator** : M. Hilchenbach, MPS, Ger.

**Objectives** : collect and analyze the chemical composition of cometary dust grains of the coma (focus on chemical classes and functional groups)

**Samples** : solid grains collected in the coma

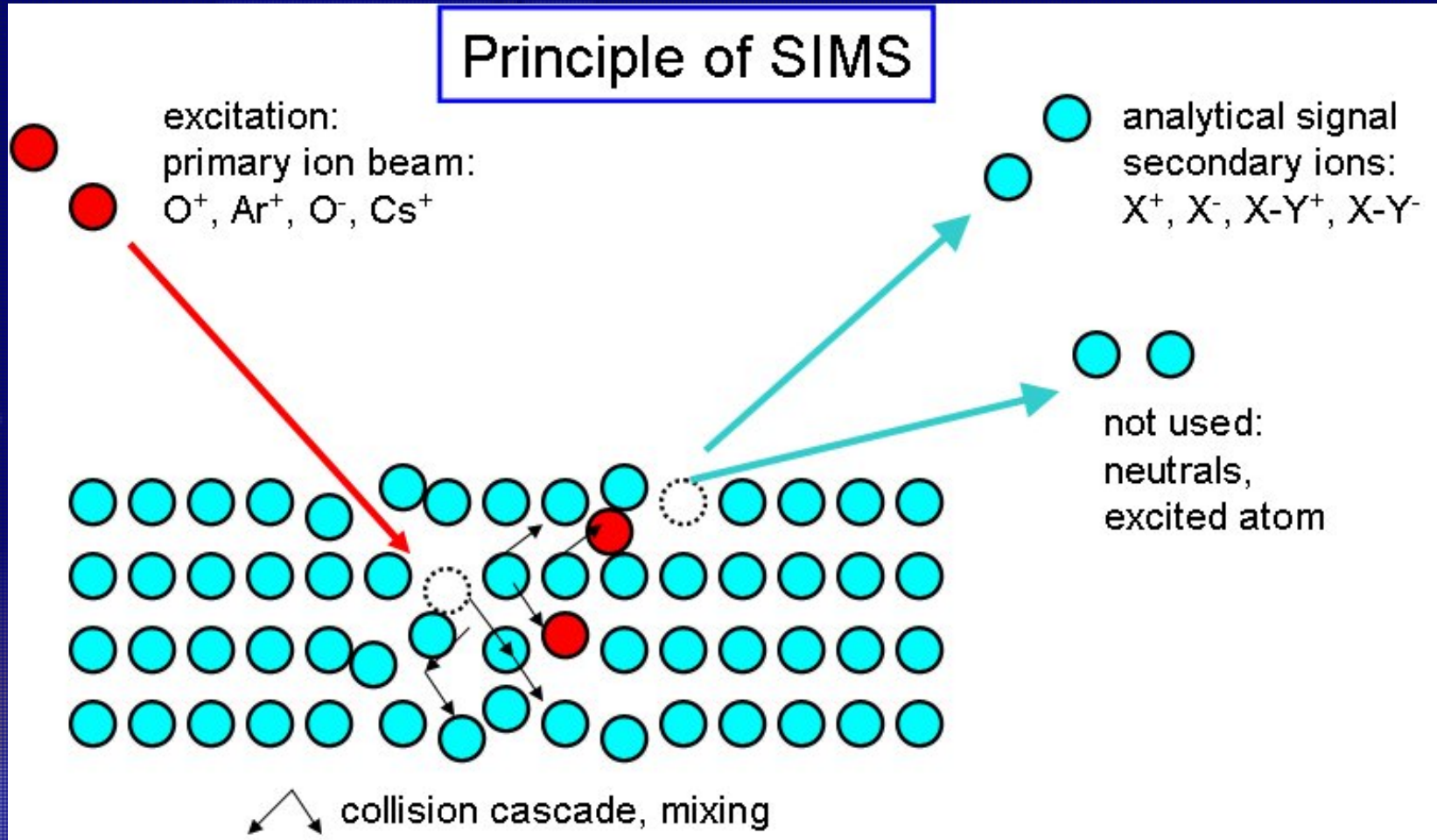
**Method** : Secondary Ion Mass Spectrometry (SIMS)

**Location** : in the Rosetta orbiter



# COSIMA

## Principle of SIMS

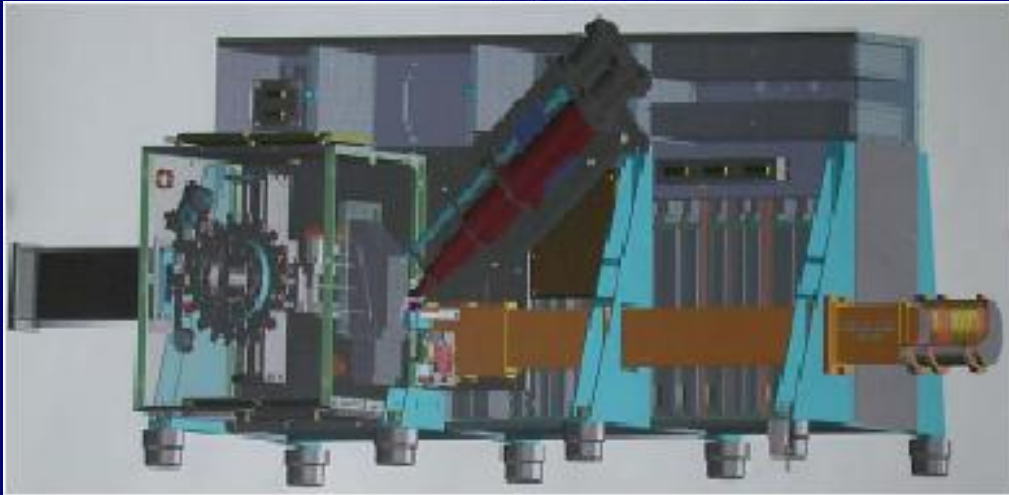




# COSIMA

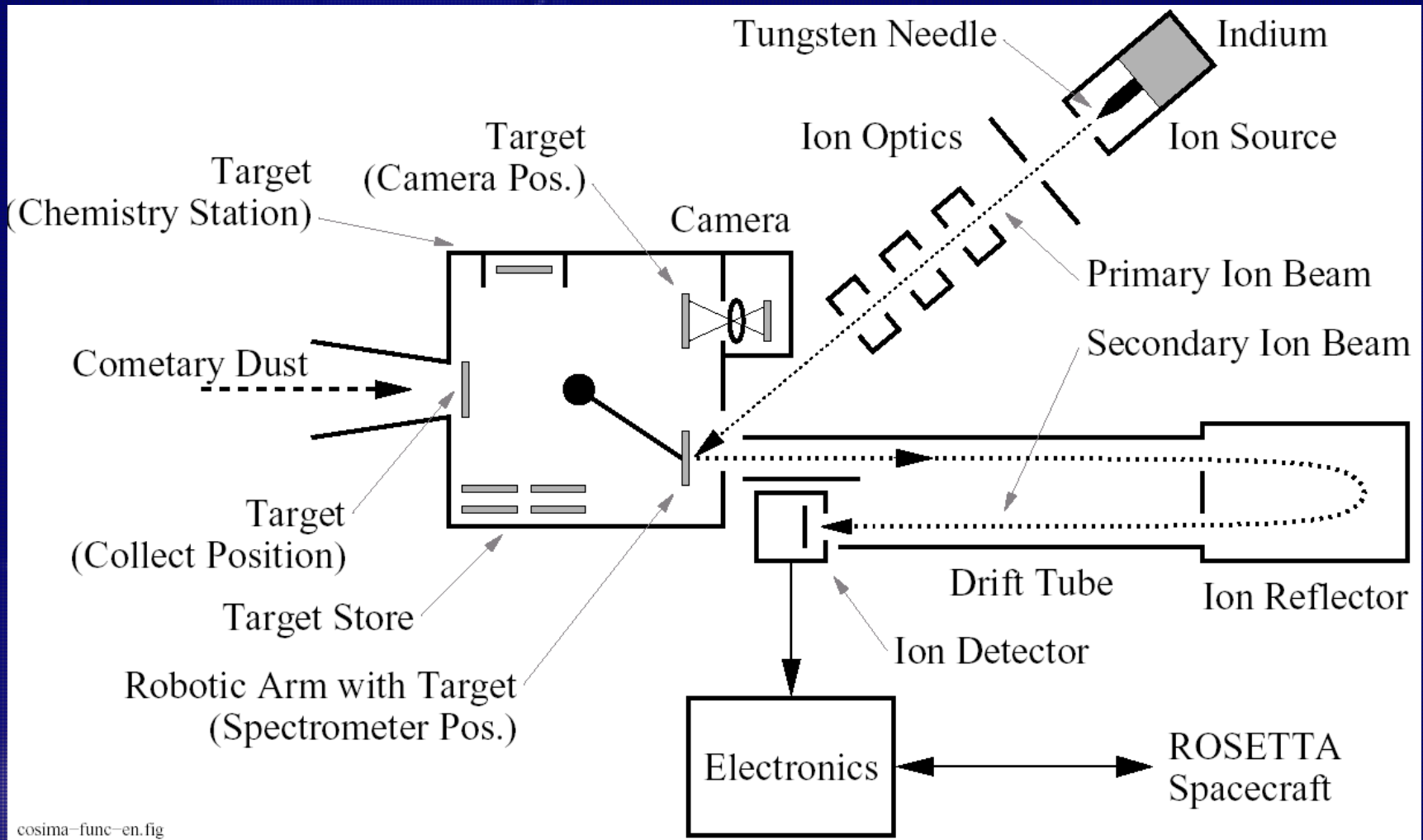
## General description

4 main parts : a dust collector, a microscope, an ion source, a mass spectrometer





# COSIMA Operations

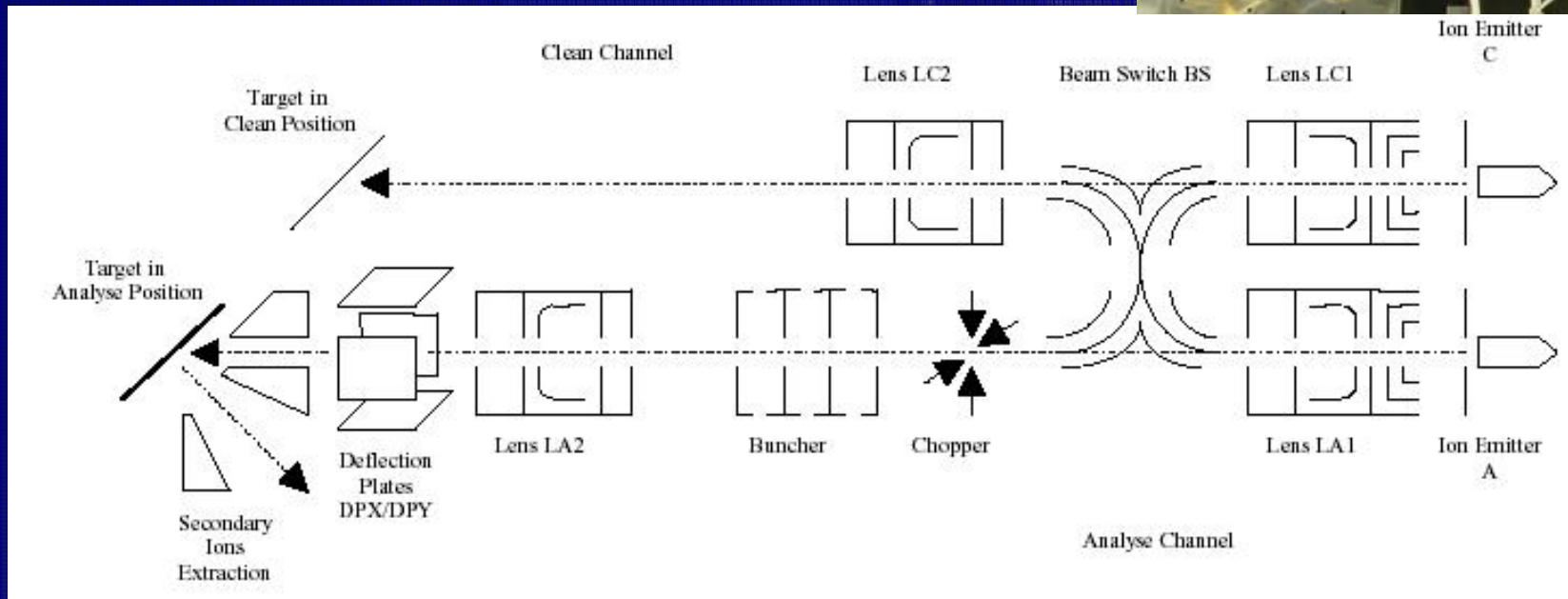




# COSIMA Ion source



## Primary Ions Beam Source



- 1 source for analysis and 1 for cleaning (sputtering)
- PIBS : ions  $^{115}\text{In}^+$ ; 1000 ions per pulse; spots diameter  $< 20 \mu\text{m}$ ;  $E=8 \text{ keV}$
- Between 10% and 0.1% of the desorbed material ionized;



# COSIMA

## Mass spectrometer

### Instrument characteristics :

Mass=19.1 kg

Dimensions : 394×973×378 mm

Mean power consumption : 20.6 W

### Mass spectrometer characteristics :

Type : Time of Flight (TOF)

Dimensions : ?/Mass : ?

Range : 1-1300 Da

Resolution :  $m/\Delta m=2000$  @ 50% for 100 Da

Source=Primary ion source emitting ions  $^{115}\text{In}^+$  (E=8 keV)

Detector=Microsphere Plate (MSP) ion detector



## Cometary Sampling and Composition

**Principal Investigator** : F. Goesmann, MPS, Ger.

**Objectives** : characterize the nature and the amount of volatile species present in the cometary nucleus, and of heavier organics (refractory ones) including their chirality properties

**Samples** : solid materials collected at the nucleus surface (& gas)

**Method** : Gas chromatography-time of flight MS (GC-TOFMS)

**Location** : in the Philae lander



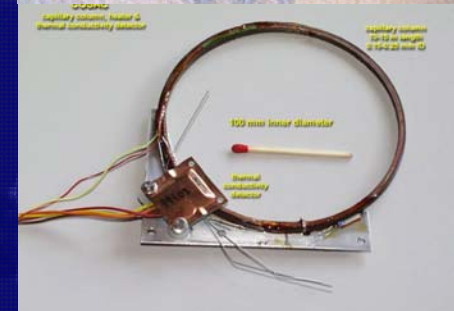
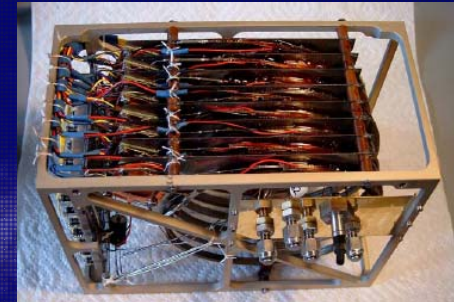


# COSAC

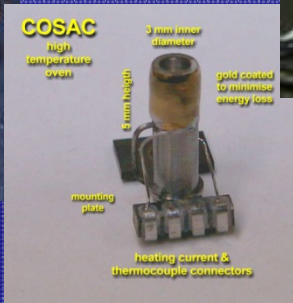
## General description

3 main parts : sampling and gas distribution and processing system, gas chromatograph, TOFMS

### Gas tanks (He)



GC



Oven and tapping station

TOFMS





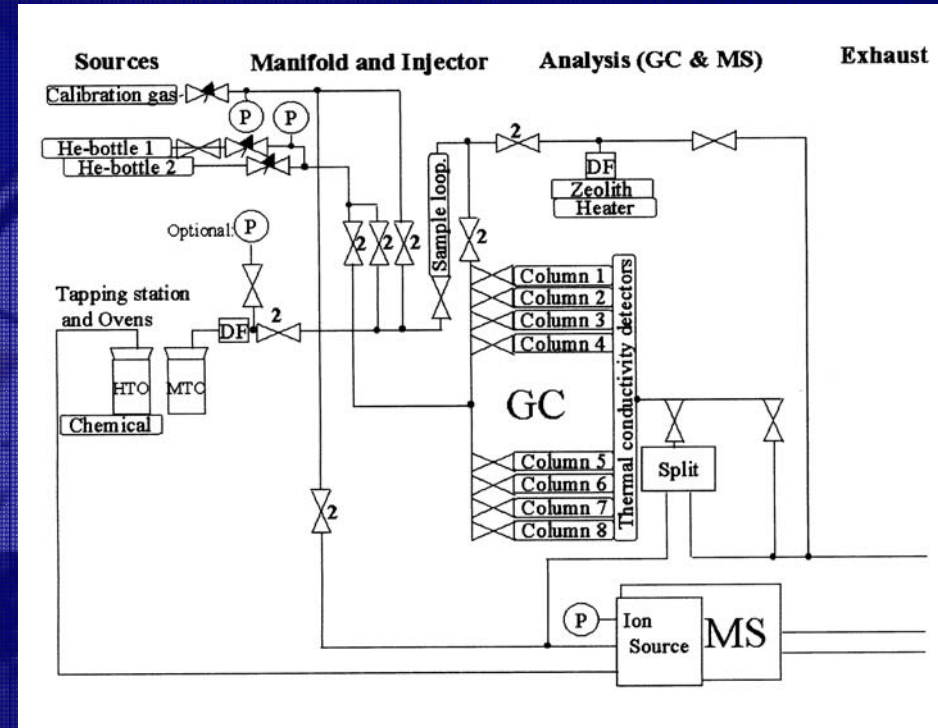
# COSAC Operations

## Sampling :

- Step pyrolysis of solids (up to 600°C)
- Derivatisation (DMF-DMA)
- Gas (direct or via Carbosieve)

## Analysis :

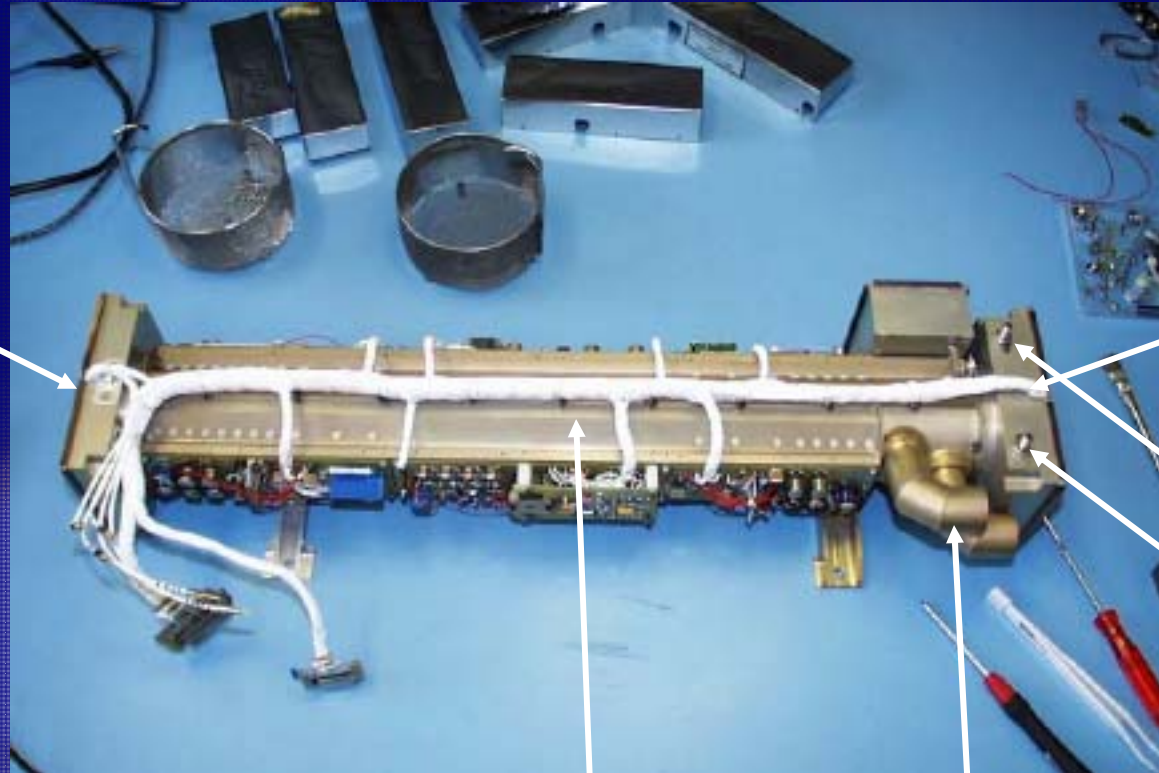
- Direct MS
- GC-MS (3 chanel for enantiomeric characterization, 5 chanel for general molecular characterization (from light inorganics to heavy organics))



Scheme of COSAC



# COSAC Mass spectrometer



Detector box

Ion source

Gas inlets

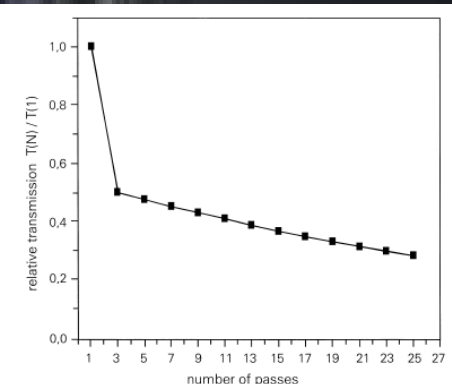
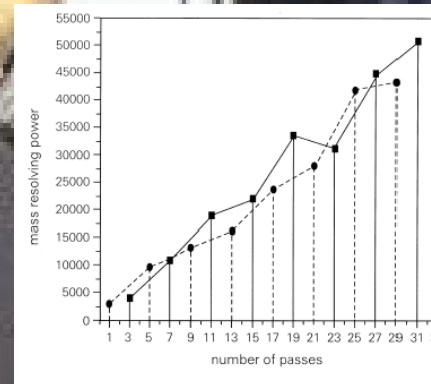
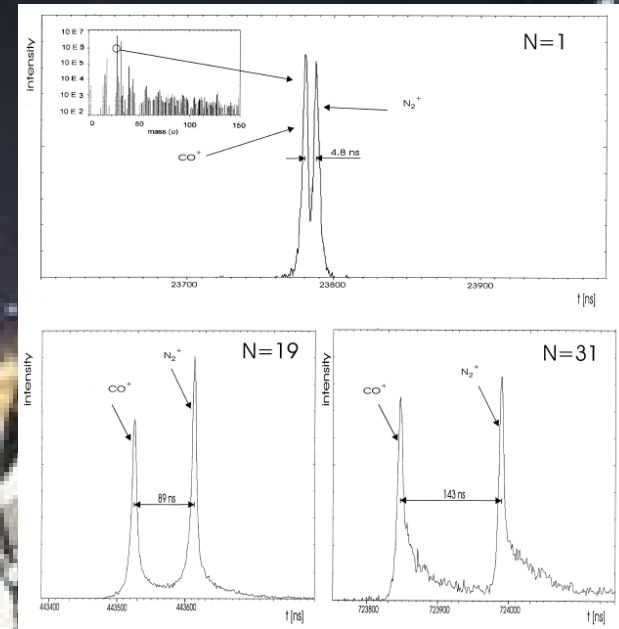
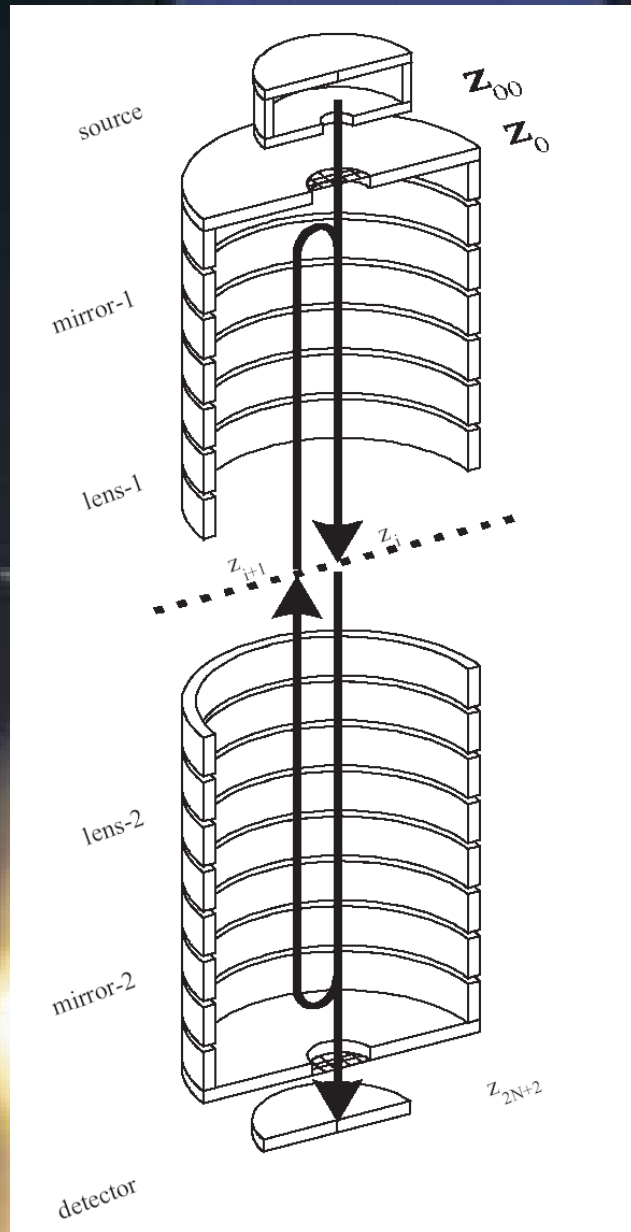
Flight tube

Exhaust pipes

Ion source= $e^-$  provided by thermal effect and generated with filaments ( $E(e^-)=70$  eV)



# COSAC Mass spectrometer



Typical performances for a 1.2 m long MS

Principle of the multi-reflexion TOF



# COSAC

## Mass spectrometer

### Instrument characteristics :

Mass=4.5 kg

Dimensions : 500×450×250 mm

Max. power consumption : 15 W

### Mass spectrometer characteristics :

Type : Time of Flight (TOF)

Dimensions : 460×80×80 mm/Mass : 1.5 kg

Range : 1-1500 Da

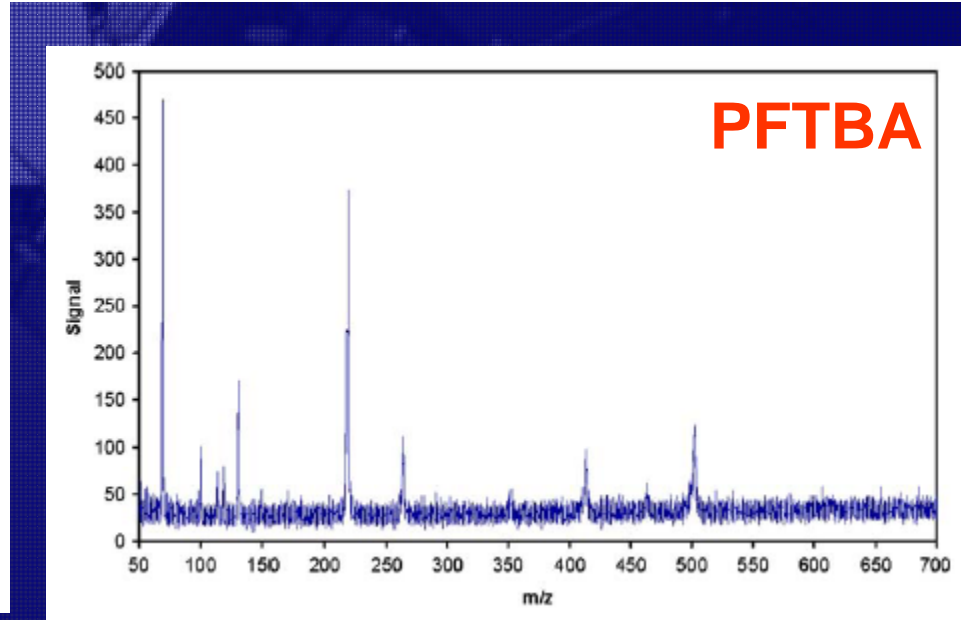
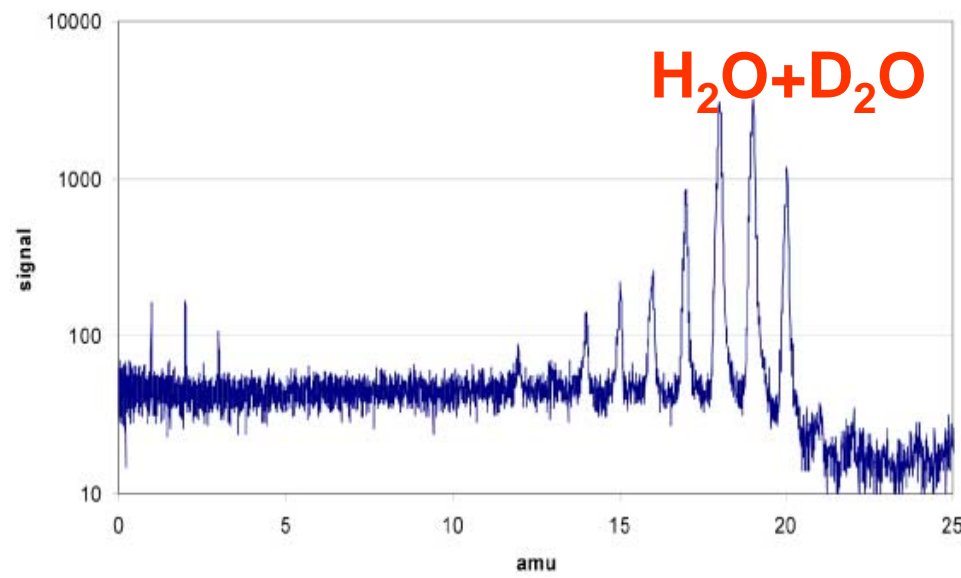
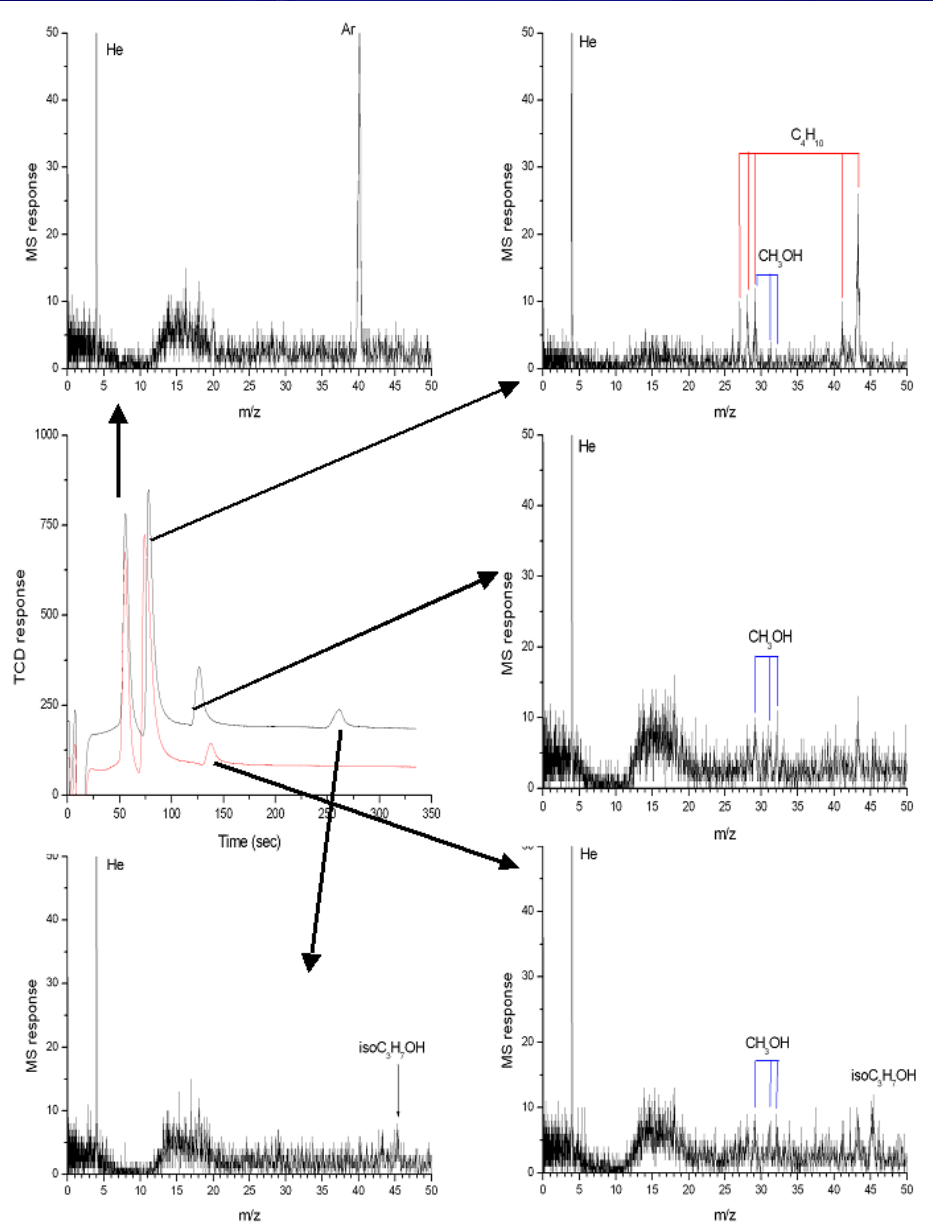
Resolution :  $m/\Delta m=350$  @ 50% for 70 Da (single path mode L=350 mm); V=1500 V

Source=e- from a heated filament of 70 eV energy

Detector=Microchannel plates (MCPs)



# COSAC : experimental results in lab





# MODULUS

Methods Of Determining and Understanding Light elements from Unequivocal Stable isotope compositions

Principal Investigator : I.P. Wright, Open Univ., UK

Objectives : characterize the nature and the isotopic (C, N, O, H) compositions of all materials present at the surface of the cometary nucleus

Samples : solid materials collected at the nucleus surface (& gas)

Method : Gas chromatography-ion trap MS (GC-ITMS)

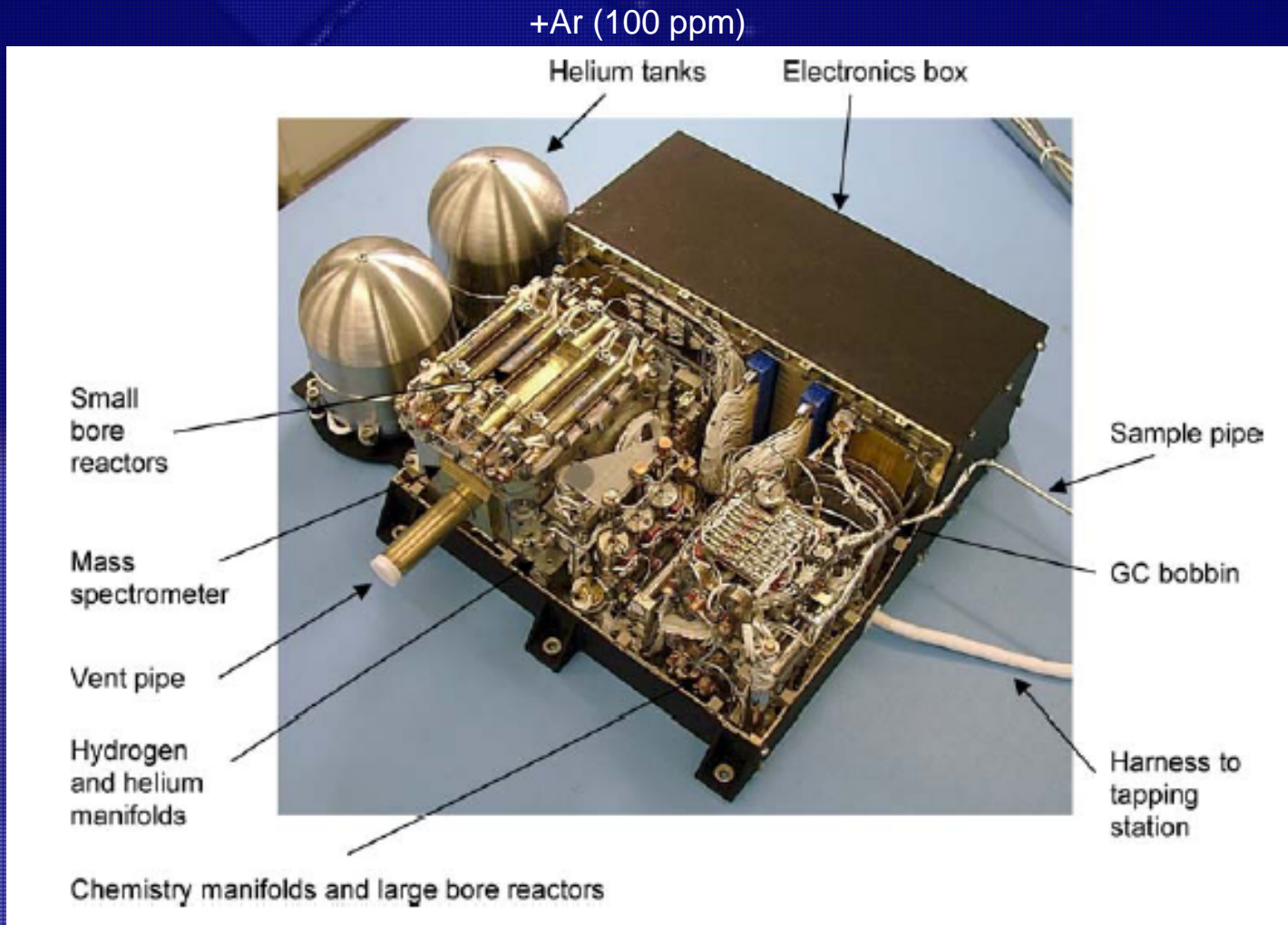
Location : in the Philae lander



# MODULUS

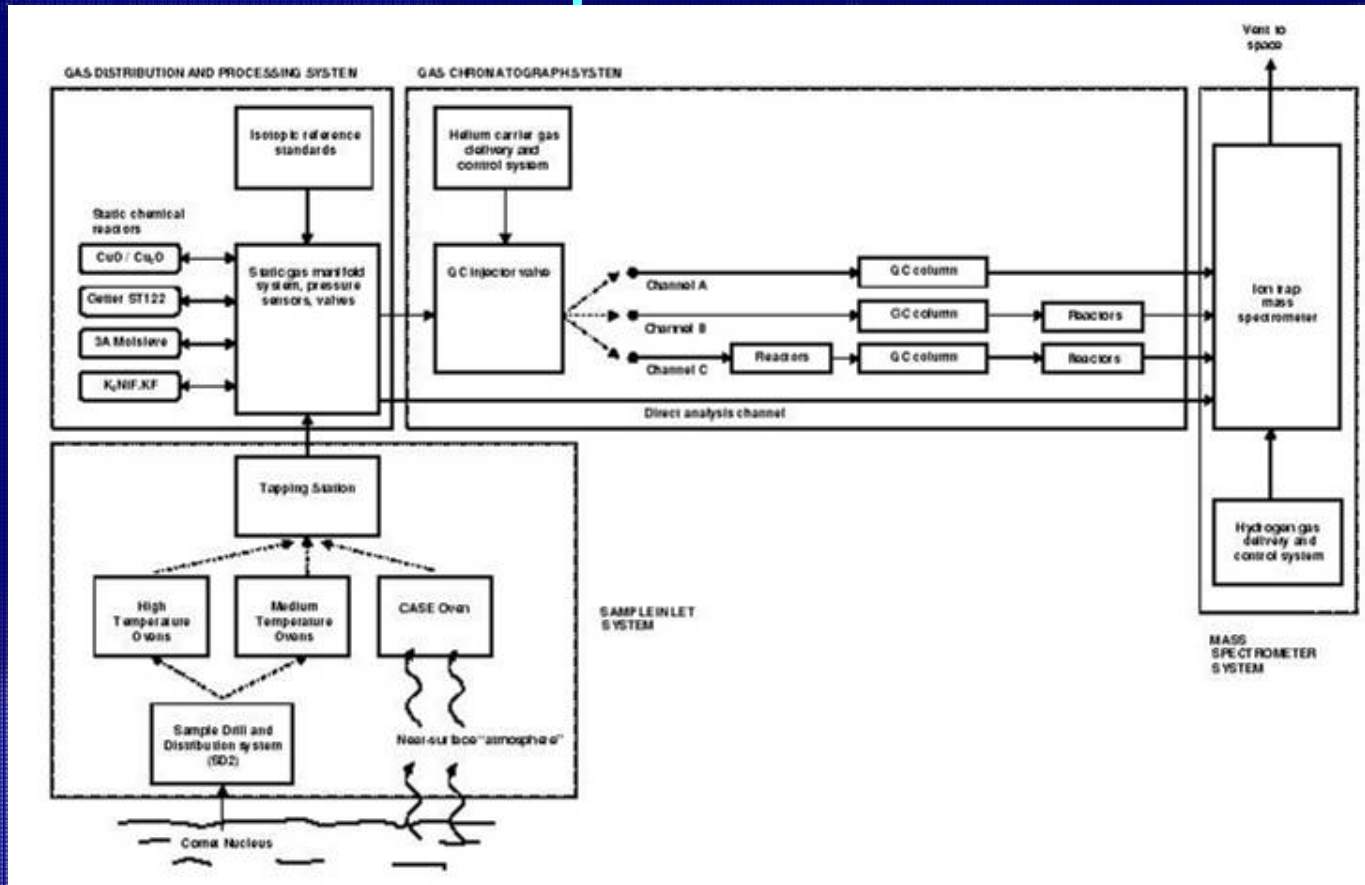
## General description

4 main parts : a sampling system, a gas distribution and processing system, a gas chromatograph, ITMS





# MODULUS Operations



## Sampling :

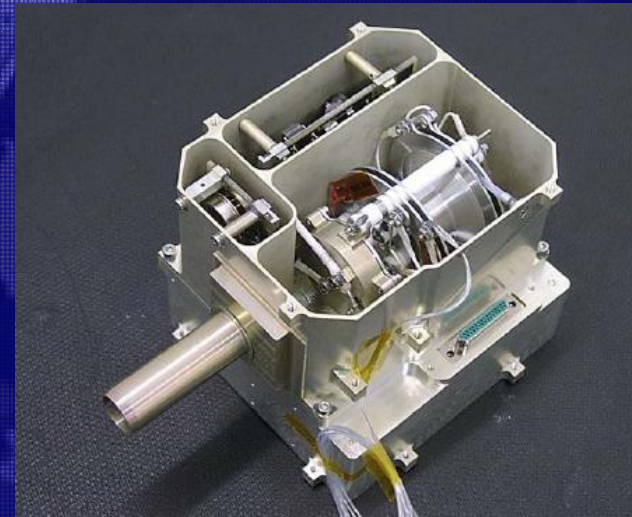
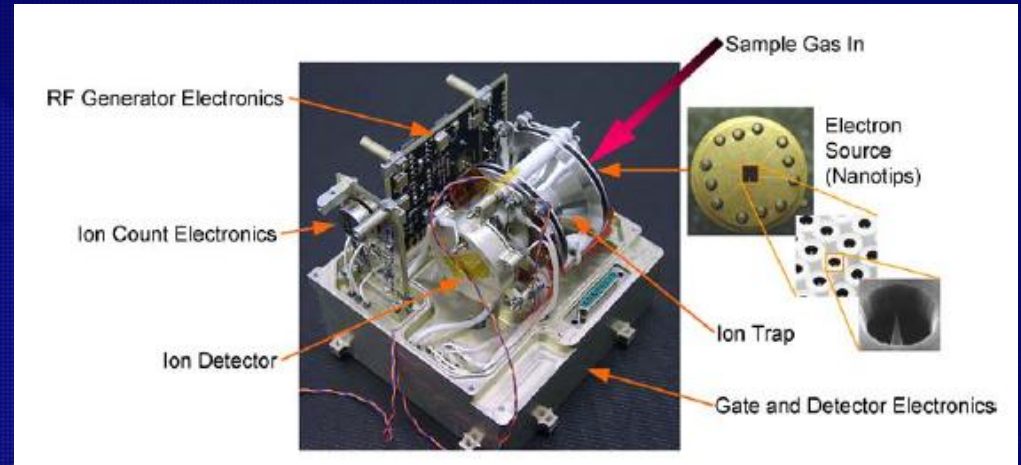
- Step pyrolysis (up 800°C)
- Combustion with O<sub>2</sub>
- Fluorination of silicates (release of O<sub>2</sub>)

## Analysis :

- Direct MS
- GC-MS (1 channel for the general composition, 1 channel for CO<sub>2</sub>, CO, CH<sub>4</sub> & N<sub>2</sub> with conversion of CH<sub>4</sub> and CO into CO<sub>2</sub>, 1 channel for H<sub>2</sub>O with a conversion into H<sub>2</sub> and CO)



# MODULUS Mass spectrometer



Species detected for isotopic measurements :  
 $N_2^+$ ,  $O_2^+$ ,  $CO_2H^+$ ,  $ArH^+$



# MODULUS

## Mass spectrometer

### Instrument characteristics :

Mass=4.5 kg

Dimensions : 250×330×110 mm

Mean power consumption : 10 W

### Mass spectrometer characteristics :

Type : Ion Trap (IT)

Dimensions : 80×100×55 mm/Mass : 500 g (75 g for IT)

Range : 12-150 Da

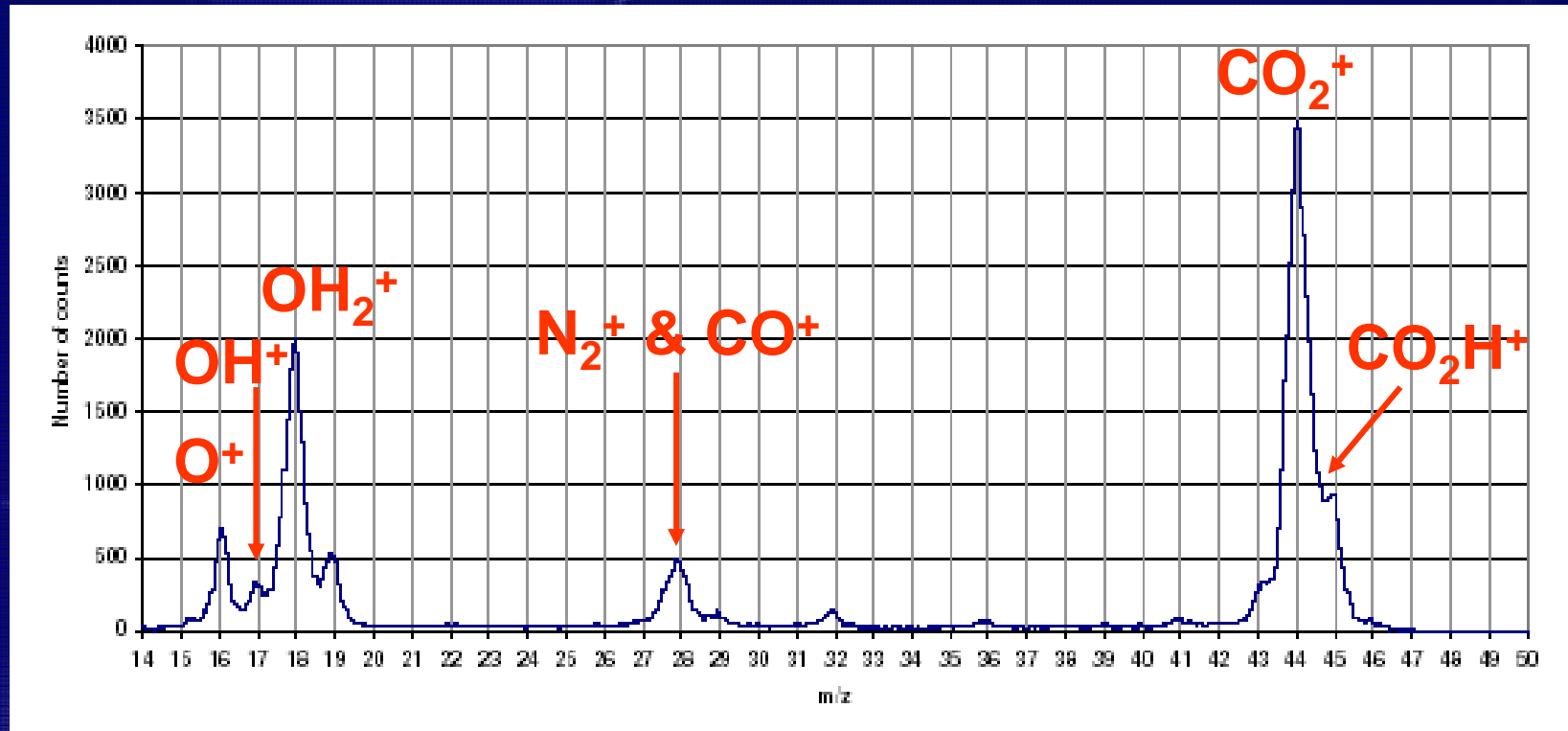
Resolution :  $m/\Delta m = ?/V = 25$  to 300  $V/RF = 0.6$  MHz

Source=e- provided by field effect generated with arrays of nanotips

Detectro=Spiral electron multiplier (built by MPS, Ger.)



# MODULUS Mass spectrometer



Example of mass spectrum recorded with MODULUS at lab  
(injection of 20 nmol of  $CO_2$ )



# MASS SPECTROMETRY IN ROSETTA

## Synthesis

MS	Sample	Type	Mass (kg) Size (mm)	Range (Da)	Resolution
COSIMA	Grains in the coma	TOF		1-1300	2000 / 50%
ROSINA	Gas in the coma	DFMS	16.2 630×630×260	12-150	3000 / 1%
		TOF	14.7 1140×380×240	1-350	>500 / 1%
COSAC	Nucleus surface material	TOF	1.5 460×80×80	1-1500	350 / 50%
PTOLEMY	Nucleus surface material	IT	0.5 80×100×55	12-150	



# Exploration of the Saturn system with the Cassini-Huygens mission (2005)

Nominal mass	Possible ion at this isobaric mass	Nominal mass	Possible ion at this isobaric mass
1	H <sup>+</sup>	26	C <sub>2</sub> H <sub>2</sub> <sup>+</sup>
2	H <sub>2</sub> <sup>+</sup> , D <sup>+</sup>	27	HCN <sup>+</sup>
3	HD <sup>+</sup> , <sup>3</sup> He <sup>+</sup>	28	N <sub>2</sub> <sup>+</sup> , CO <sup>+</sup> , C <sub>2</sub> H <sub>4</sub> <sup>+</sup>
4	He <sup>+</sup>	29	<sup>13</sup> CO <sup>+</sup> , C <sup>17</sup> O <sup>+</sup> , <sup>15</sup> NN <sup>+</sup>
5		30	NO <sup>+</sup>
6		31	
7	Li <sup>+</sup>	32	O <sub>2</sub> <sup>+</sup> , SO <sub>2</sub> <sup>+</sup>
8		33	
9		34	H <sub>2</sub> S <sup>+</sup> , O <sup>14</sup> O <sup>+</sup>
10		35	
11		36	<sup>36</sup> Ar <sup>+</sup> , HCl <sup>+</sup>
12	C <sup>+</sup>	37	
13	<sup>13</sup> C <sup>+</sup>	38	<sup>38</sup> Ar <sup>+</sup> , <sup>37</sup> HCl <sup>+</sup>
14	N <sup>+</sup> , N <sub>2</sub> <sup>+</sup>	39	K <sup>+</sup>
15		40	Ar <sup>+</sup> , Ca <sup>+</sup>
16	O <sup>+</sup> , O <sub>2</sub> <sup>+</sup> , CH <sub>4</sub> <sup>+</sup>	41	<sup>41</sup> K <sup>+</sup>
17	OH <sup>+</sup> , NH <sub>3</sub> <sup>+</sup>	42	Kr <sup>+</sup>
18	H <sub>2</sub> O <sup>+</sup>	43	
19	HDO <sup>+</sup> , F <sup>+</sup>	44	CO <sub>2</sub> <sup>+</sup> , N <sub>2</sub> O <sup>+</sup>
20	Ne <sup>+</sup> , HF <sup>+</sup>	45	<sup>13</sup> CO <sub>2</sub> <sup>+</sup> , <sup>13</sup> C <sup>17</sup> OO <sup>+</sup>
21		46	NO <sub>2</sub> <sup>+</sup> , C <sup>18</sup> OO <sup>+</sup>
22	CO <sub>2</sub> <sup>+</sup> , <sup>22</sup> Ne <sup>+</sup>	47	
23	Na <sup>+</sup>	48	
24		49	H <sub>2</sub> SO <sub>4</sub> <sup>+</sup>
25		50	

## MS main specifications :

Nature :            Quadrupole

Mass :                ~4 kg

Volume :            ~20 cm<sup>3</sup>

Power :              12 W

m/z range :        1-46

Resolution :

Sensitivity :        N/A



# SW/Plasma MS Timeline

Mass Spectrometer	Year, Mission	Resolution
Ion Traps	1959 Luna 1	< 2
Faraday Cup	1961 Explorer 10	~2
Electrostatic E/Q	1962 Mariner 2	~3
Wien Filter	1983 ISEE-3	~5
Magnetic Sector	71 Apollo*, 86 Giotto*	>40, >10
Linear TOF	1984 Ampte	~15
Isochronous TOF	1996 Wind	~100
Reflectron TOF	2004 Rosetta*	>3000
Helical TOF	20??	>1000

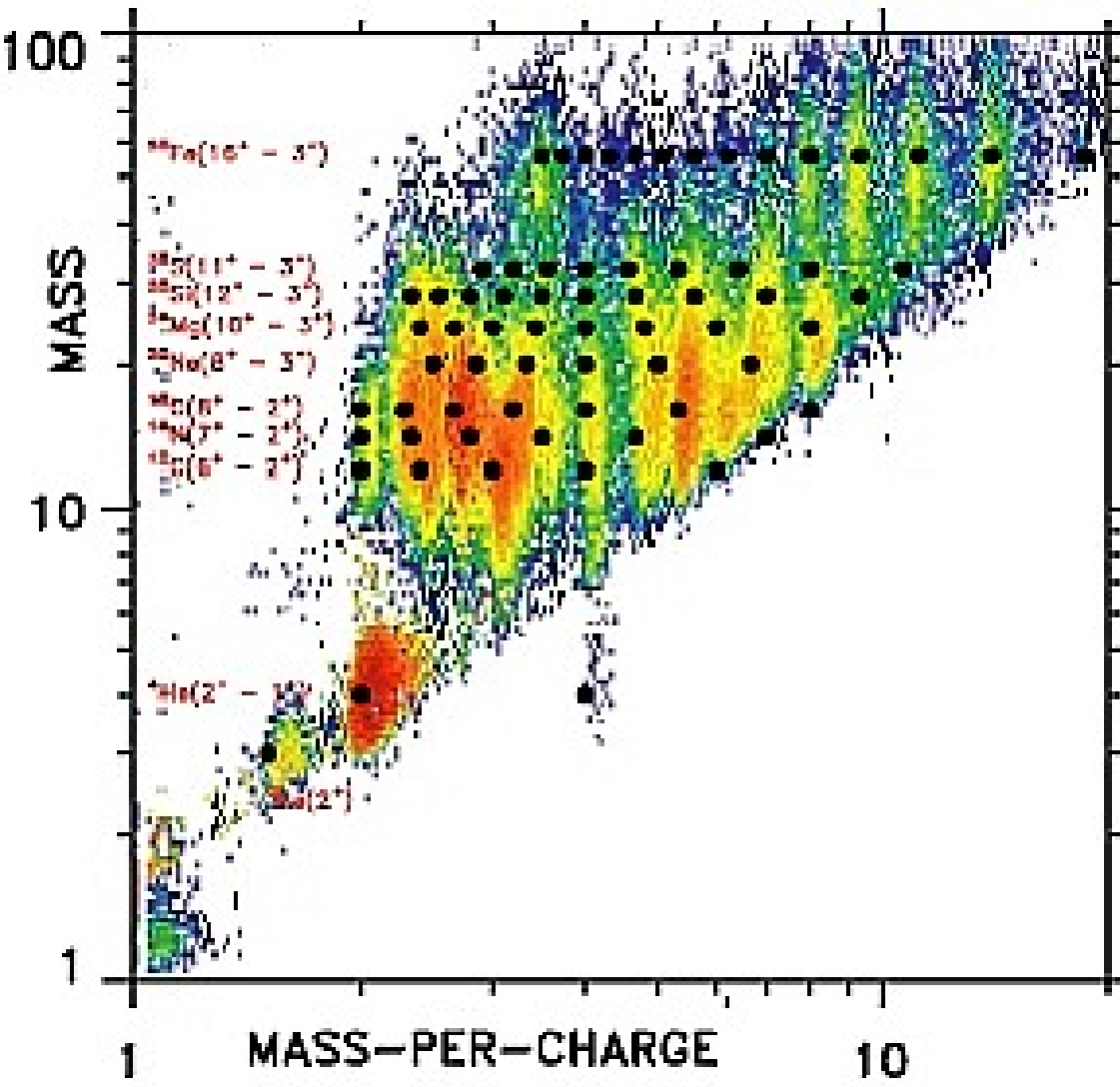


# Why Bother with Composition?

- “Minor effects of minor ions” said a colleague
- The Plasma Ecosystem
  - Origins: tracers
    - Fast/slow solar wind, ionosphere/SW m’spheric
  - Acceleration: both as tracer and trigger
    - O+ changes reconnection rate;
  - Transport: both tracer and differentiator
    - SEP composition reveals E/q acceleration
  - Death: ENA visualizations (IMAGE)
    - He from SW, O from Earth



# SW Elemental Composition



Mass can separate degenerate M/Q species

Charge states give coronal temperatures at different altitudes.

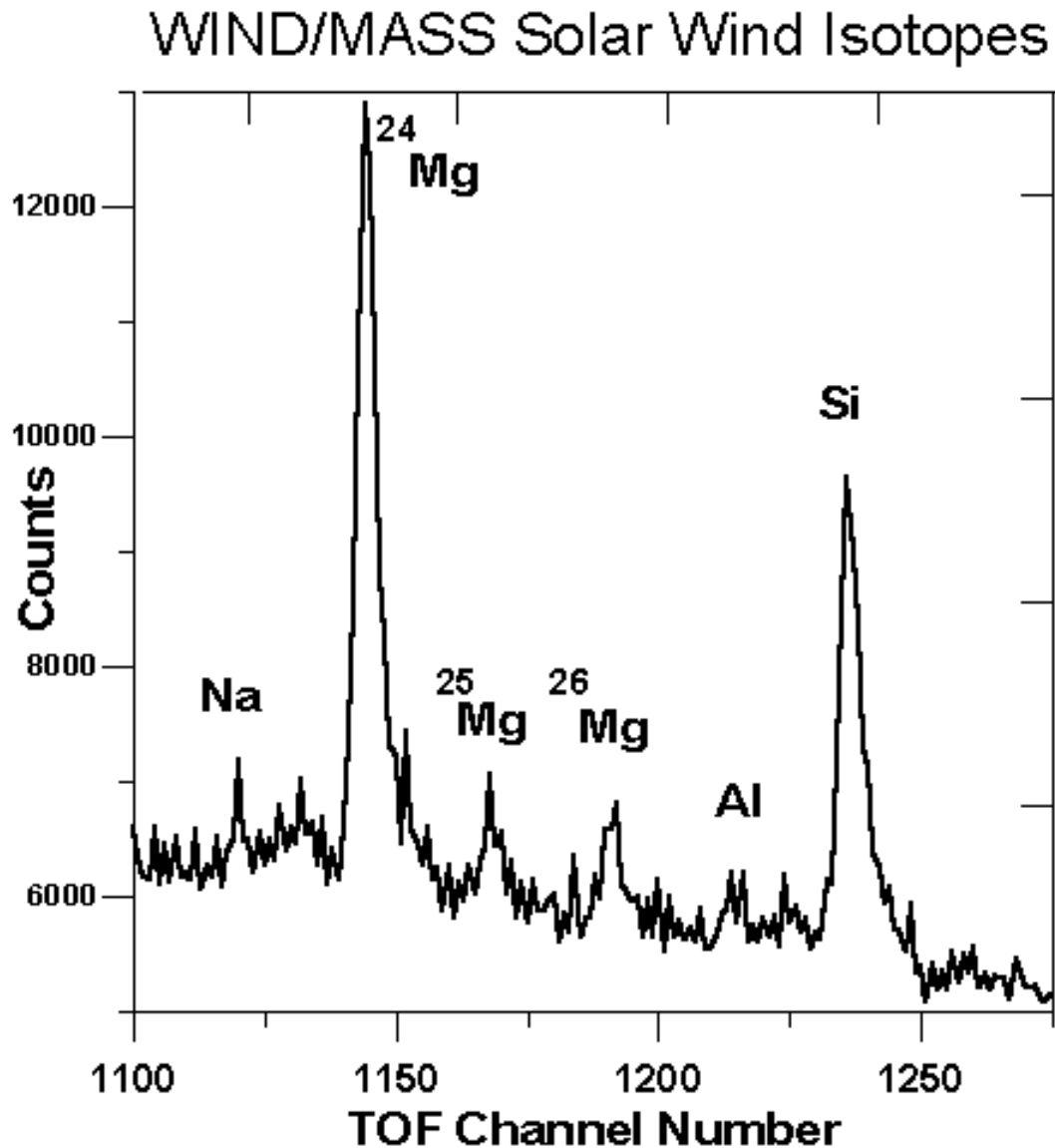
Differentiate

Fast/Slow SW

Ascertain SW origins



# SW Isotopic Composition



Isotopes can reveal unique acceleration in SW.  $^3\text{He}$ ,  $^{15}\text{N}$ .

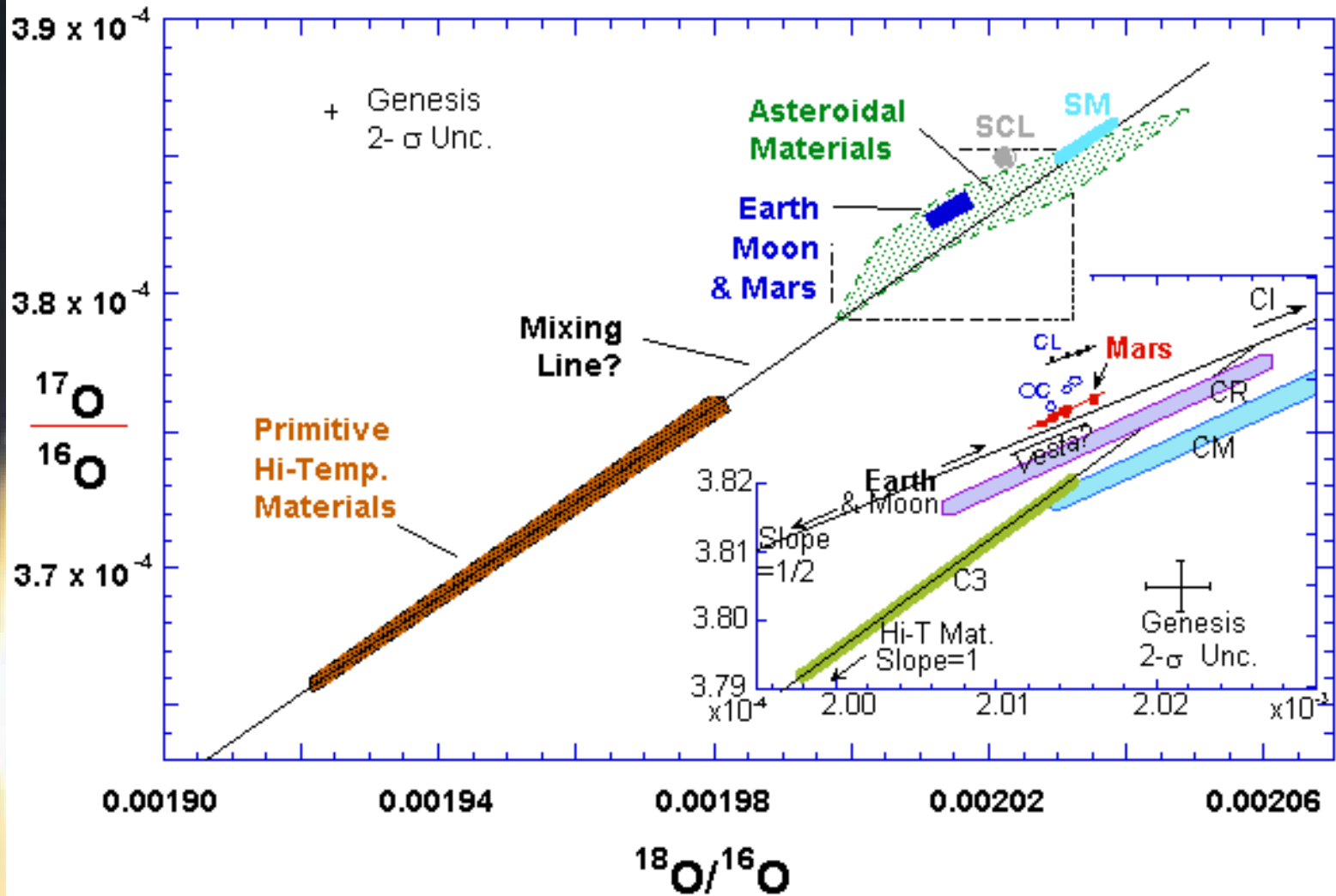
Triple Mg isotopes permit studies of mass fractionation of Solar interior.

Origins of proto-solar nebulae, age of the sun.



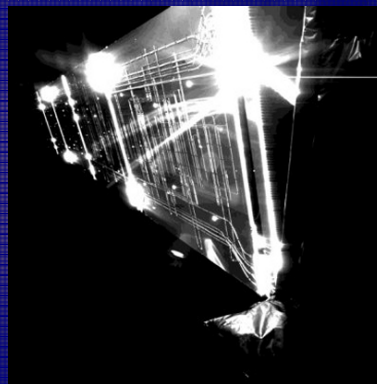
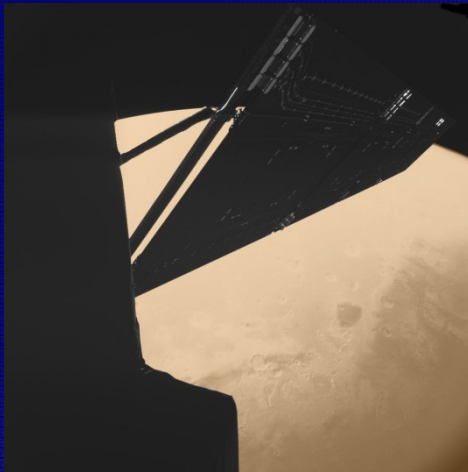
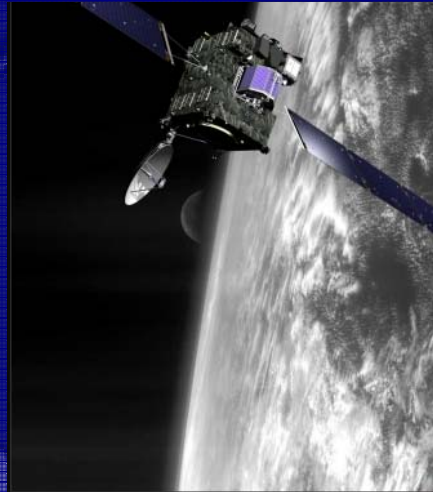
# Origins of Solar System

## Oxygen Isotope Map of the Solar System





# The Rosetta mission Timeline



03/2004 Launch

03/2005 Earth flyby

02/2007 Mars flyby

11/2007 Earth flyby

09/2008 21 Lutetia fly-by

11/2009 Earth flyby

07/2010 2867 Steins flyby

Mid 2014 Rendez-vous  
with comet P67CG

11/2014 Philae release

06/2015 Perihelion passage

12/2015 End of the mission



# The Rosetta mission

## The orbiter



### 11 instruments :

ALICE } UV, vis & IR spectroscopy  
VIRTIS }

OSIRIS vis, near IR&UV camera

CONSERT Sounding of the interior  
of the nucleus

COSIMA } Mass spectrometry  
ROSINA }

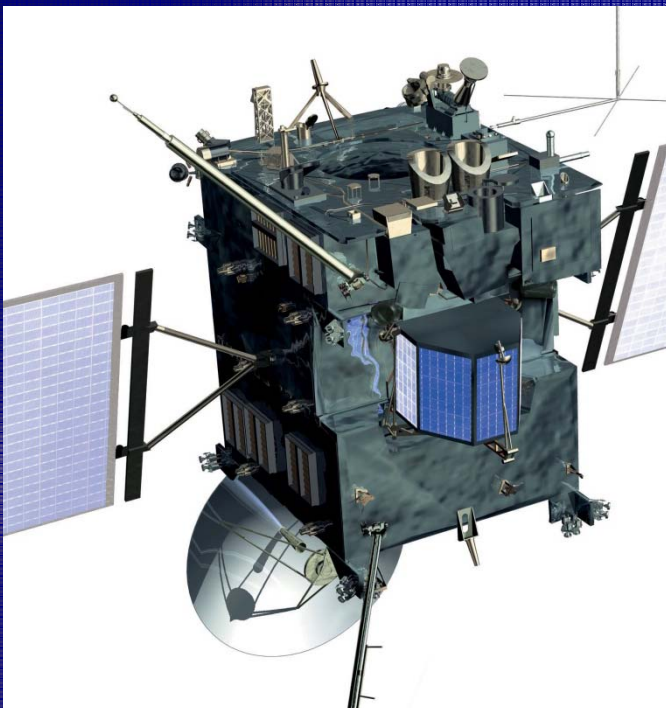
MIRO Microwave instrument

GIADA Instrument for dynamic  
and morphology of dust grains

MIDAS AFM for dust grains  
observations

RPC Plasma measurements

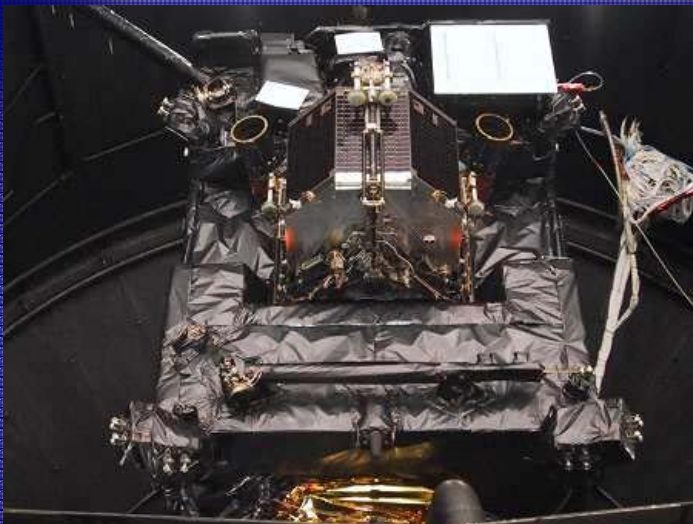
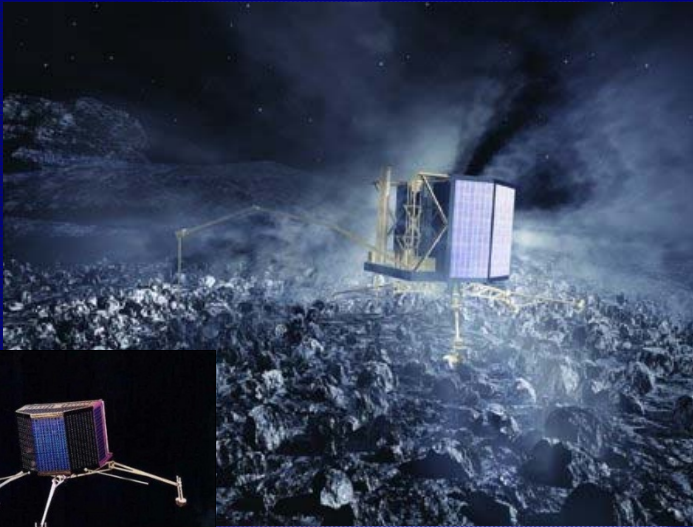
RSI Radio science (spacecraft)





# The Rosetta mission

## Philae : the lander



### 9 instruments :

**COSAC** GCMS for molecules

**MODULUS-Ptolemy** MS for isotopes

**CONSERT** sounding of the interior  
of the nucleus

**APXS** APX spectrometer

**MUPUS** penetrator

**ROMAP** magnetometer and plasma  
monitor

**SESAME** electric properties of the  
surface

**CIVA** visible and IR micro cameras

**ROLIS** camera



# Choice of techniques appropriate to space mass spectrometry

	Mass Range	Mass Resolution FWHM	Sensitivity	Duty Cycle	Complexity (sensor+ electronics)	Technology Readiness	Example
Quadrupole	<150	~150	High	Low	Low	High	Cassini/ Huygens
Magnetic	<150	~2500	Medium	Low	High	High	Rosetta/ DFMS
TOF	>>100	~2500	High	High	Medium	High	Rosetta/ RTOF
Ion trap	>100	>100	High?	Low	Medium	High	Rosetta lander
MBTOF	>>100	>10,000	High	High	High	Medium	SwRI MBTOF