INVESTIGATION OF VOLATILES *IN SITU* IN REGOLITH DURING PHOBOS SAMPLE RETURN, LUNA-RESOURCE, AND LUNAR-GLOBE MISSIONS

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An outline

- sources of volatiles in the Moon polar regions
- gas analytical complex for the Phobos Sample Return and the Lunar-Globe and Lunar-Resource missions

Moon

Apollo- and Lunar- landers samples

Water 64 ppb – 5 ppm ([McCubbin et al., 2010])

Carbon 0÷400 ppm ([Simoneit et al., 1973])

Nitrogen 0÷150 ppm ([Simoneit et al., 1973])

Volatile rich samples

61221,7 ([Wszolek et al., 1973])

H_2O (119 ppm), CO_2 (35 ppm), CO (10 ppm), NO, HCN (4 ppm), hydrocarbons C_nH_{2n+z} , n=1 to 6, z=2 to -4, (CH_4, 0.4 ppm, C_2H_4, 3.4 ppm) oxygenated species $C_nH_{2n+z}O$, n=1 to 4, z=2 to -4, and nitrogenous species $C_nH_{2n+z}N$, n=1 to 3, z=0 to -4.

Carbon-rich layers

300 nm layer	carbon up to 60% ([Dikov et al., 1999])
100 nm layer	carbon up to 16% ([Hashizume et al., 2002])

Polar regions?

Possible sources of polar volatiles deposition on the Moon

1. **DEGASSING OF THE INTERIOR**

   Information about endogenous activity
   Information about bulk volatiles inventory

2. **DEGASSING DUE TO HYPERVELOCITY IMPACTS OF METEORITES AND COMETS**

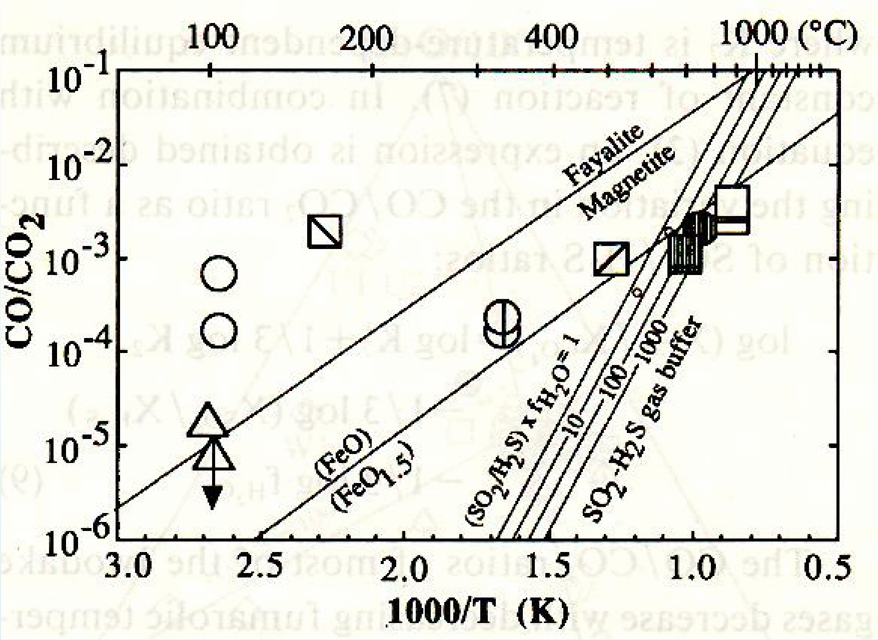
   Information about exogenous activity
   Dynamics of volatiles due to impacts

3. **INTERACTION OF SOLAR WIND PROTONS WITH OXYGEN OF SURFACE ROCKS**

   Information on solar wind and airless body interaction

“Volcanic” gases

Carbon containing components: CO_2, CO, HC



CO/CO_2 ratio in volcanic gases for some Japanese volcanoes [Shinihara et al., 1993]

Sulfur containing components: SO_2, H_2S, S_n

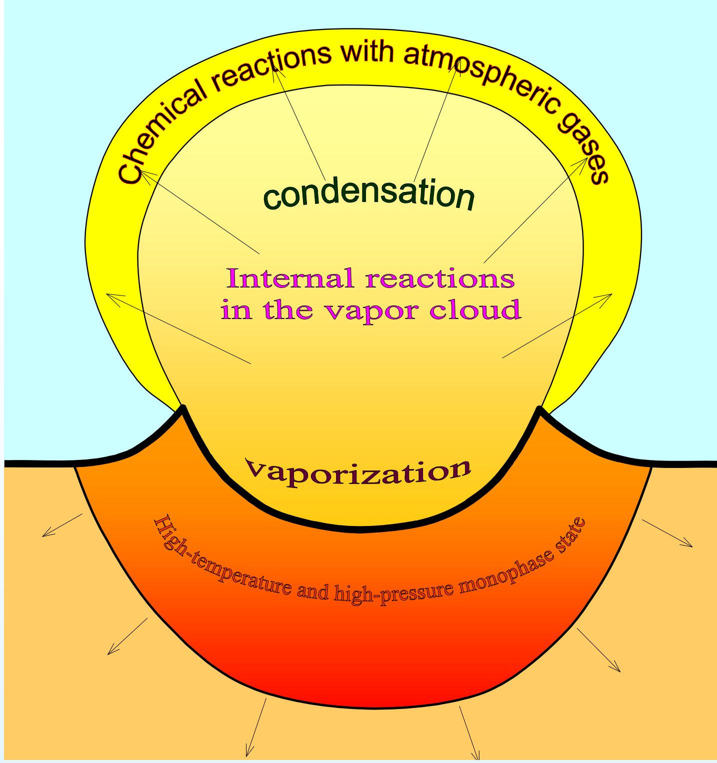
ORGANIC COMPOUNDS IN VOLCANIC ERUPTIONS

Organic compounds discovered in vapor mixture from boreholes of thermal fields.

[Porshnev et. al., 1983]

Groups of compounds	Subclasses, individual compounds and its approx. content
Alkanes	pentane, i-pentane, hexane (15-25 ppm), heptane (13-20 ppm), octane (9-16 ppm), nonane (6-9 ppm), decane (2-7 ppm), undecane (8 ppm);
Cycloalkanes	cyclohexane, methyl-cyclohexane;
Aromatic hydrocarbons	benzene (1560-2028 ppm), toluene (652-750 ppm), ethyl-benzene (26-39 ppm), n-xylene (30-47 ppm), m-xylene (144-196 ppm), o-xylene (90-154 ppm), propyl-benzene (3-6 ppm), C_3-benzene (36-65 ppm), C_4-benzene, naphthalene (61-201 ppm) etc.

Hypervelocity impacts



Main components: H_2, O_2, H_2O, CO, CO_2,

Carbon containing components:

CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, CH_3CHO, C_3H_6, C_3H_4, $C_4H_{2\text{-}10}$, C_5H_x, C_6H_6, HCN, CH_3CN,

Nitrogen containing components:

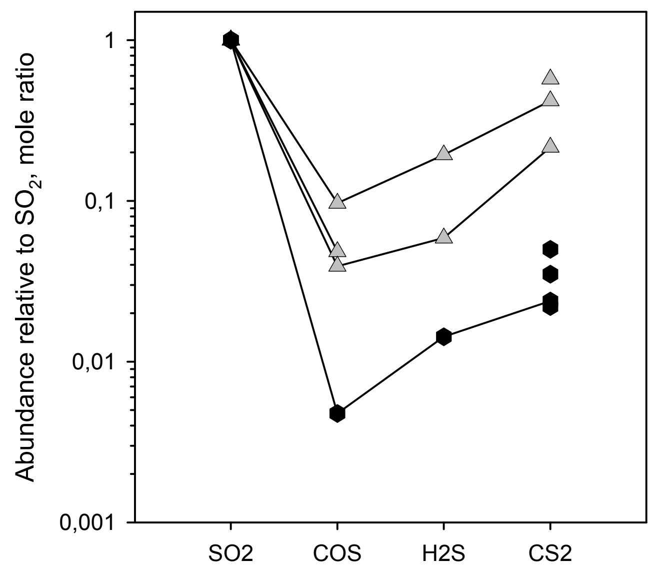
N_2, NO_x, HCN, CH_3CN

Sulfur containing components:

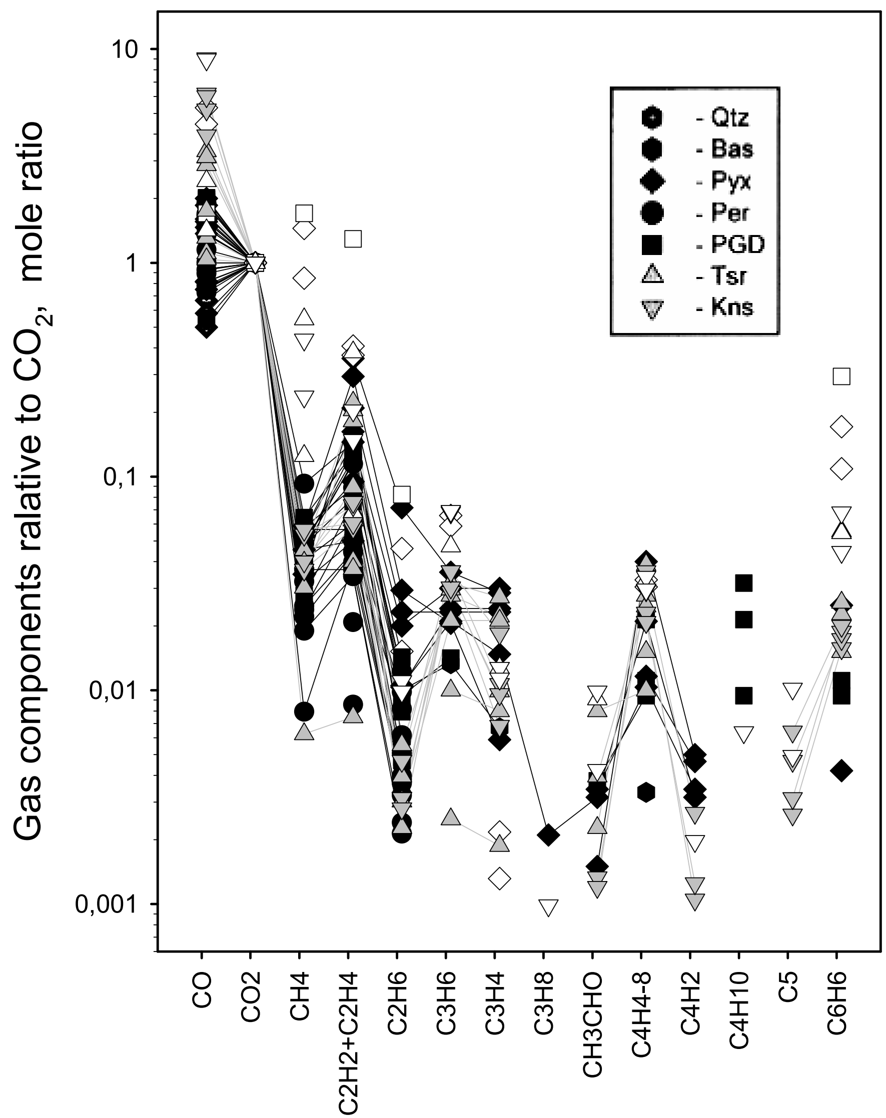
SO_2, CS_2, COS, H_2S,

Stability of gas pattern of impact-induced gas mixtures

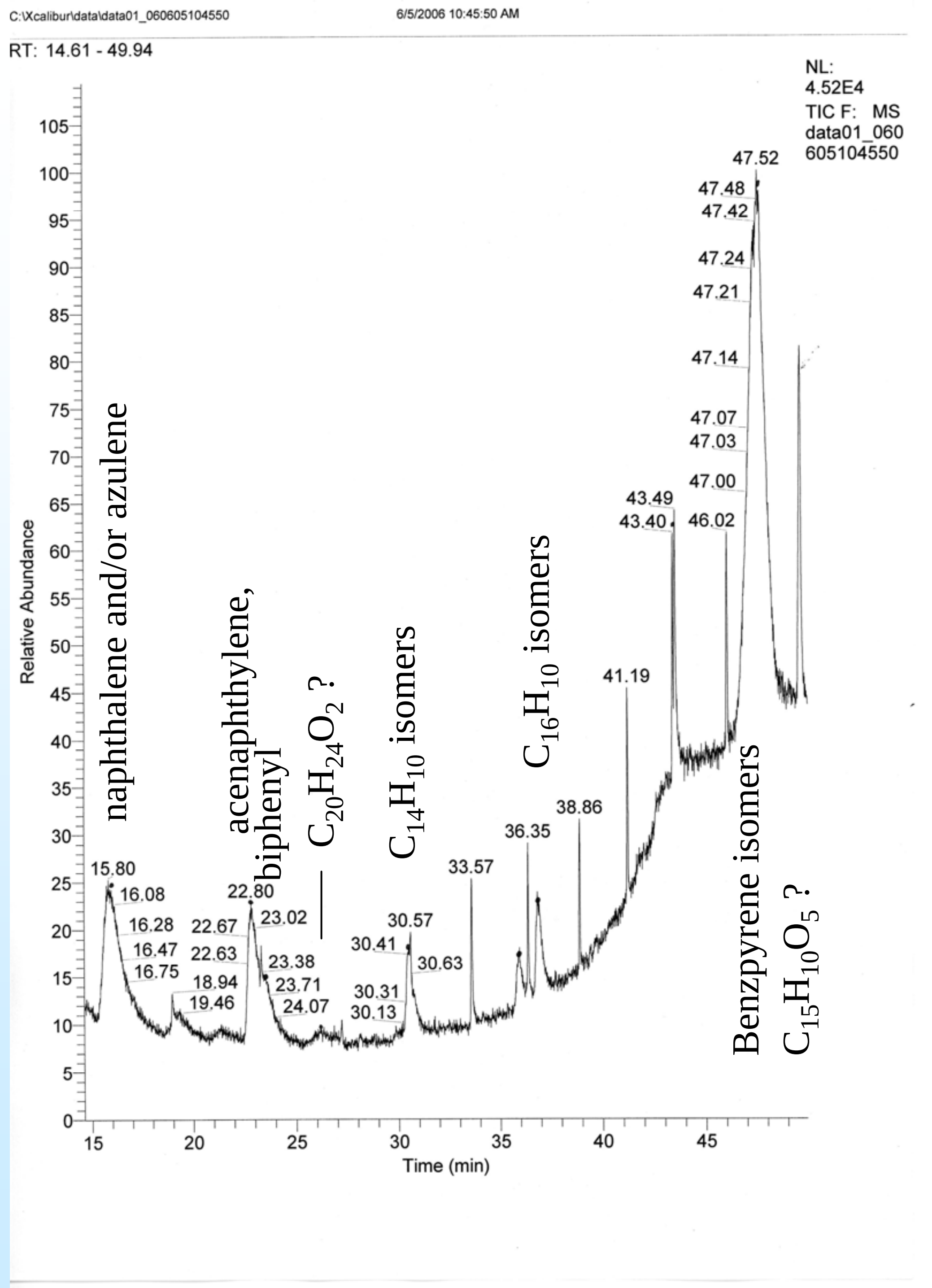
Composition of carbon-containing gases relative to CO_2 in LP experiments in helium and in hydrogen (open symbols)



A pattern of S containing gases relative to SO_2 in experimentally obtained gas mixtures.



The chromatogram of organics extracted from the condensed phase in LP experiment on vaporization of augite in CH_4 atmosphere. *(anlysis of B.A.Rudenko)*



INTERACTION OF SOLAR WIND PROTONS WITH OXYGEN OF SURFACE ROCKS

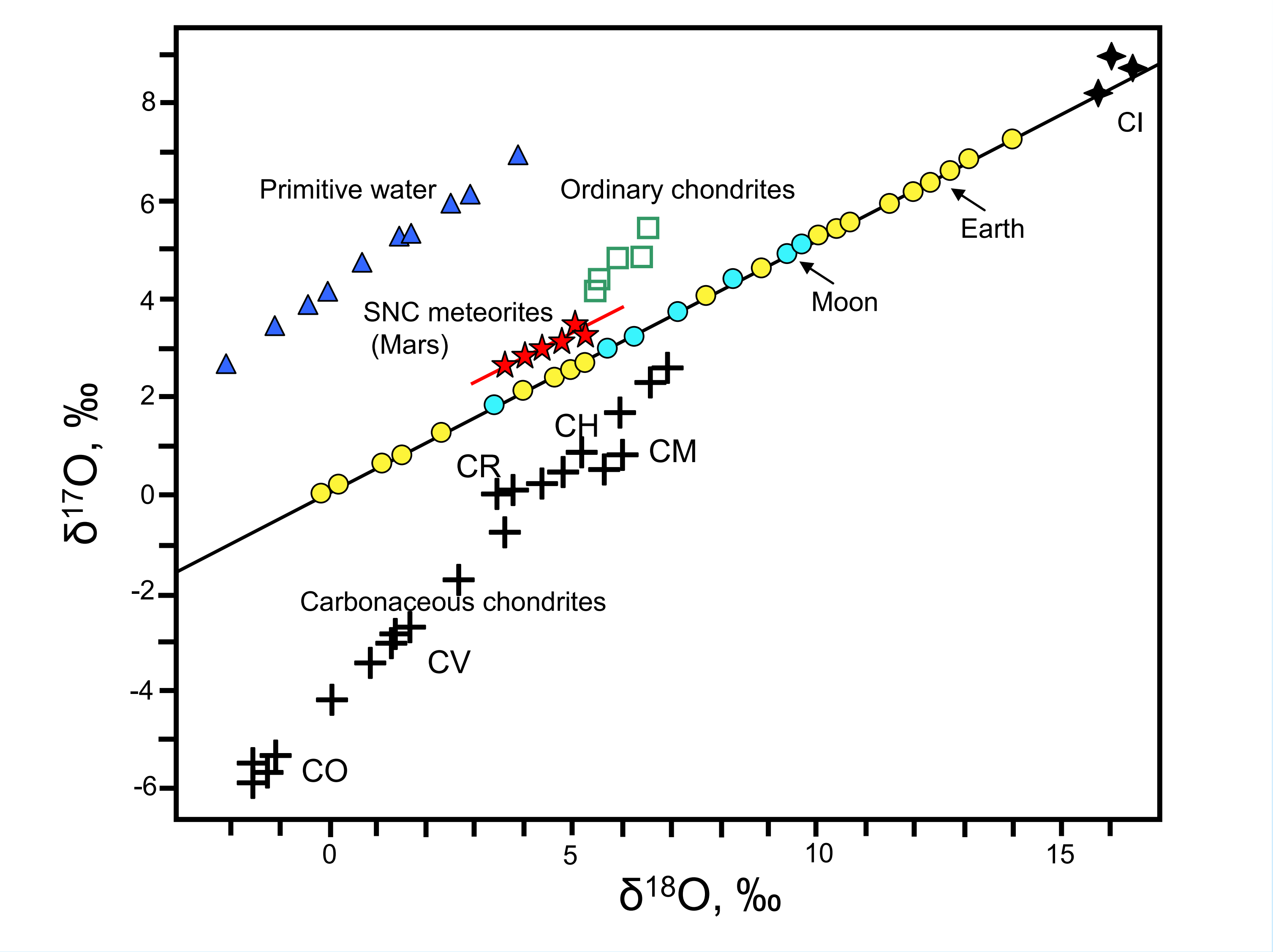
$$2H_{sw} + O_{MeOx} \rightarrow H_2O$$

Polar volatiles are mainly pure H_2O with isotopic ratios:

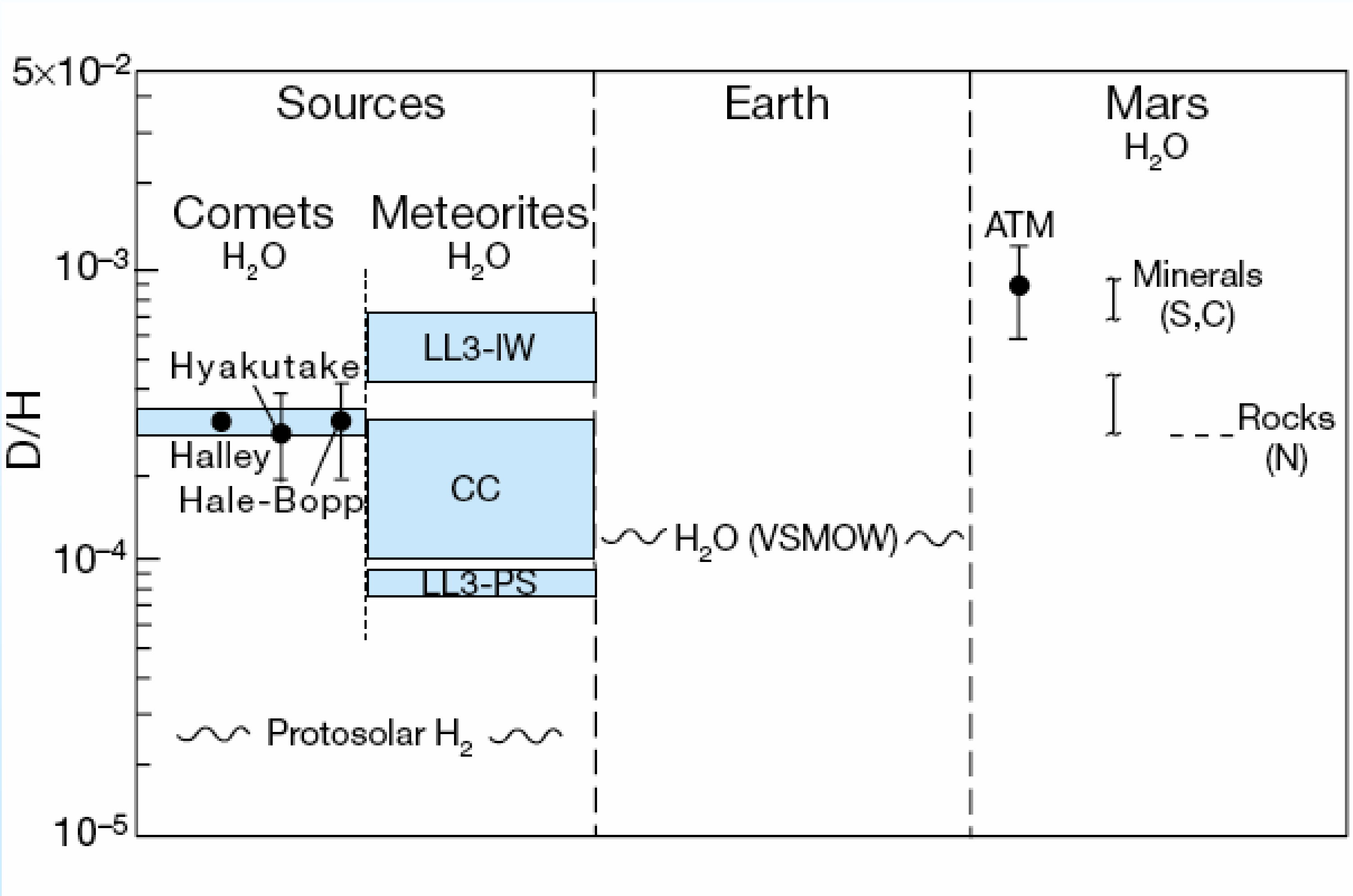
D/H = solar

$^{18}O/^{17}O/^{16}O$ = rocks

Oxygen isotopes in the Solar System



Hydrogen isotopes in the Solar System



SIGNIFICANCE OF POLAR VOLATILES INVESTIGATION

Dominant H_2O is indicative of the **solar wind** input

CO/CO_2 <10, dominant SO_2 and H_2S for sulfur containing gases, high aromatic compounds concentration for organics (?) are indicative for **volcanic activity**

CO/CO_2 ~ 1, significant CS_2 and COS concentrations for sulfur containing gases, high concentration of alkenes (C_2H_2, C_2H_4 !) for organics are indicative for the **hypervelocity impacts** input

Isotopic ratios D/H and $^{18}O/^{17}O/^{16}O$ are indicative for the **source** of volatiles

Comprehensive investigation of volatiles is necessary

Phobos Sample Return mission (2011)

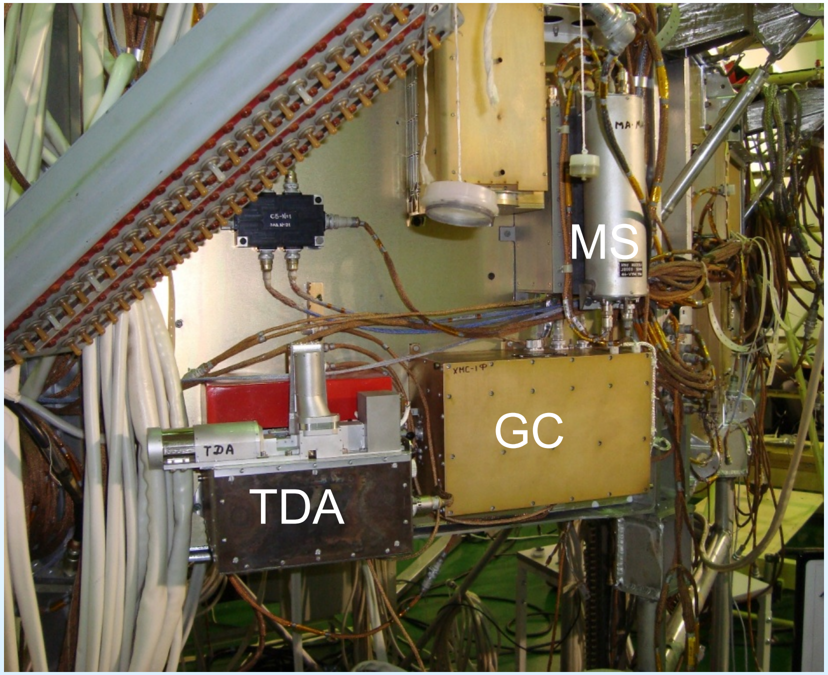
Scientific objectives of the "PhSR" mission

- to investigate the origin of Martian satellites on example of Phobos;
- to investigate properties of small planetary objects in space environment;
- to study possible differentiation of early planetary materials;
- **to study volatiles inventory;**
- **to study organic materials;**
- to study the influence of Phobos on the near Martian environment (dust torus, gas, plasma and magnetic field perturbations);
- to investigate the detailed structure of the Martian atmosphere including vertical profiles of temperature, aerosol, and trace atmospheric components (water vapor, CO, CH_4, etc);
- to investigate diurnal variations of surface temperature of Mars.

Gas Analytic Package (GAP) for the "Phobos Sample Return Mission"

Scientific objectives of the GAP

1. Investigation of chemical composition and inventory of volatiles (water, CO_2, N_2, SO_2, organics, noble gases, etc.) *in situ* in the soil at the landing place;
2. Investigation of volatile-containing phases in the soil of the Phobos;
3. Investigation of organic components in the soil of the Phobos;
4. Measurement of isotopic composition of CHON elements ($^{13}C/^{12}C$, D/H, $^{17}O/^{16}O$, $^{18}O/^{16}O$, $^{15}N/^{14}N$) and noble gases;
5. To constrain the mineralogical composition of the Pobos soil (with emphasis on the volatile-bearing minerals) on the basis of thermal and gas evolving experiments with the use of data from other experiments.



The structure of the GAP

Soil preparation and loading system → Thermal Differential Analyzer → Chromatograph → Mass-spectrometer

Problems of regolith sampling

Phobos Sample Return Mission

The goal: Investigation of volatiles in bulk rocks

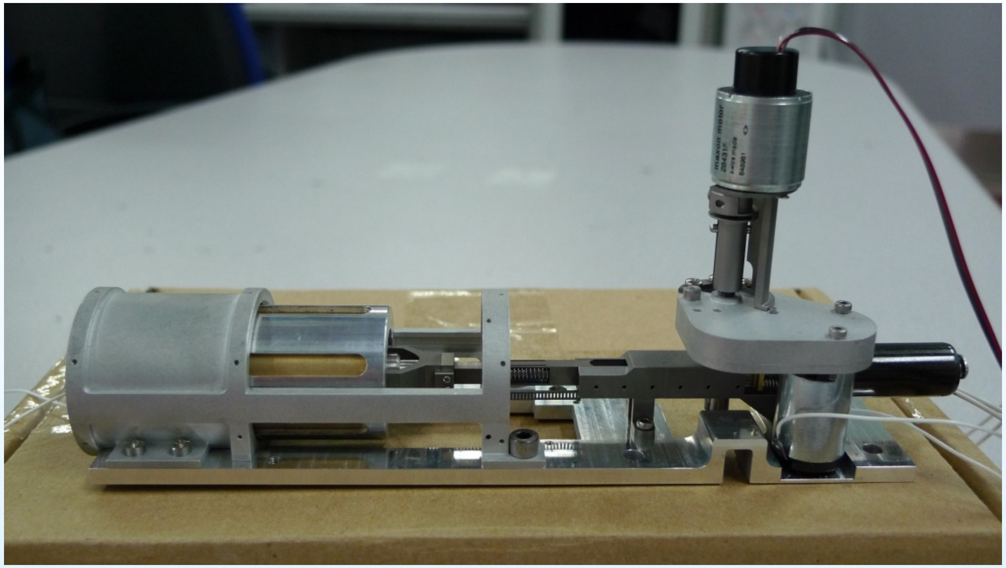
The action: To sample undifferentiated pieces of rocks and mill them to fine grain state to facilitate evolution of gases during heating

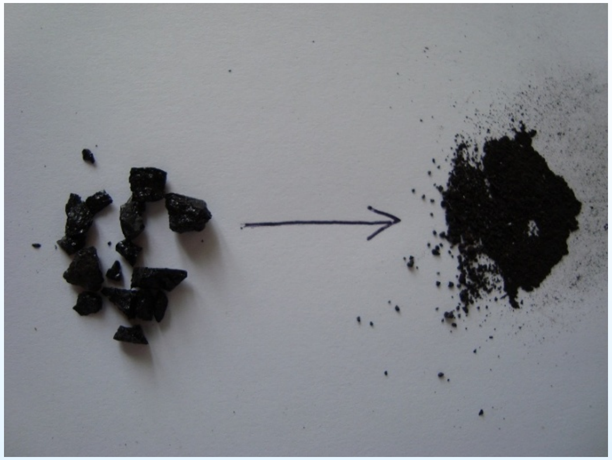
Lunar-Resource and Lunar-Globe Missions

The goal: Investigation of volatiles which most probably are frozen on surface of regolith grains

The action: To sample fine grain fraction of regolith under the temperature of deposition

SOil Preparation SYStem = SOPSYS





Tasks of the device

1. To take a portion of soil from the manipulator.
2. To mill large pieces of rocks and sieve the soil to extract the necessary fraction for loading into pyrolytic cells.
3. To extract the dose of the sample for loading into the pyrolytic cell.
4. To clean itself for the next cycle.

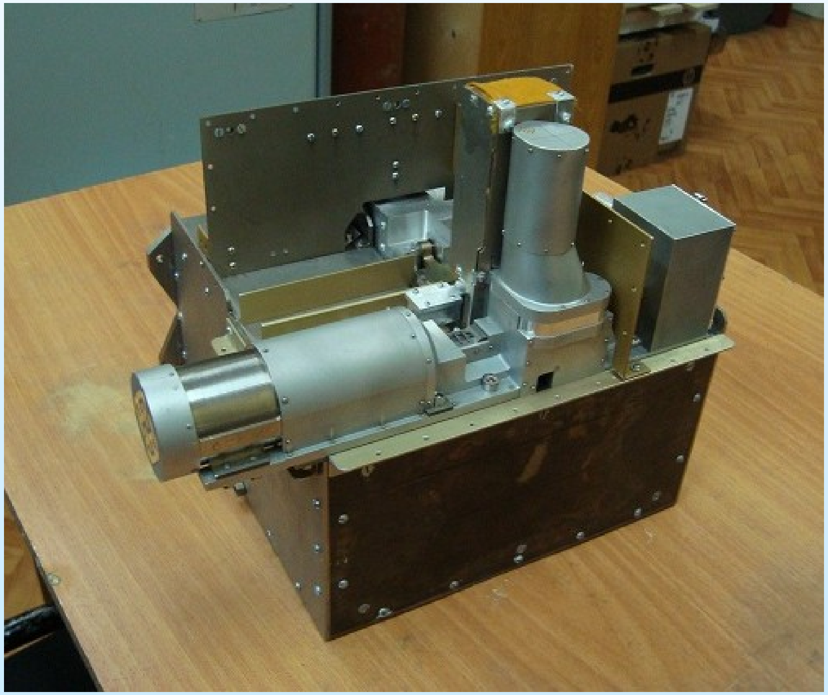
Thermal Differential Analyzer (TDA)

Scientific objectives of the TDA

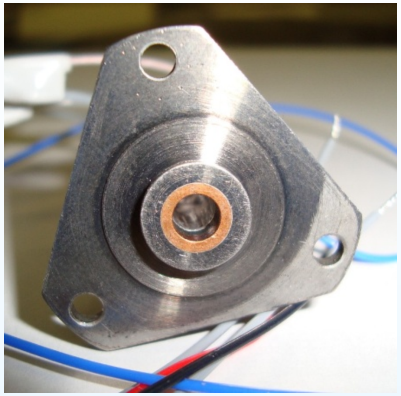
1. To measure exo- and endothermal reactions in the sample of soil to determine minerals with phase transitions at temperatures <1000°C;

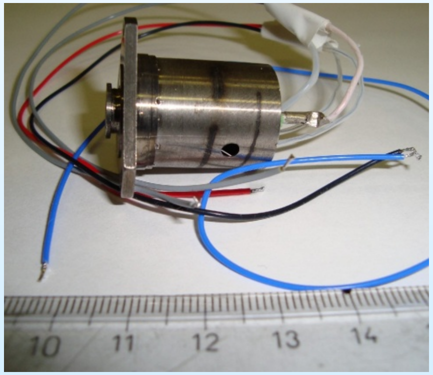
2. To perform the release of volatile components into the gas phase and provide their transfer into GC and MS;

3. To perform pyrolysis of heavy organics (kerogens?) for their analysis in GC and MS;



Pyrolytic cell

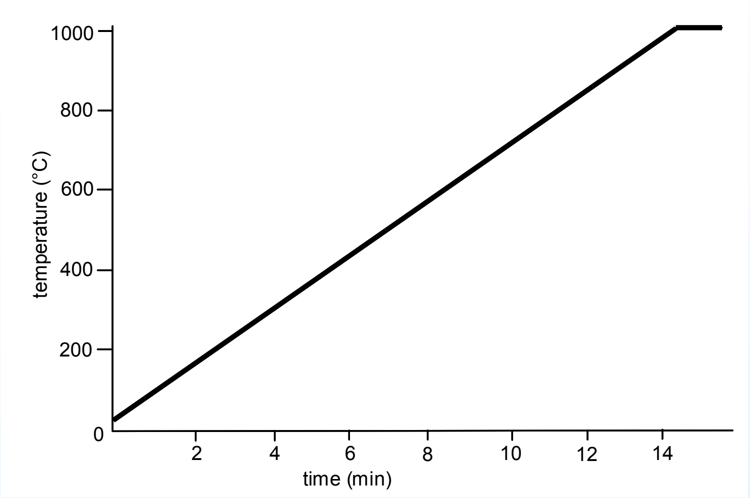


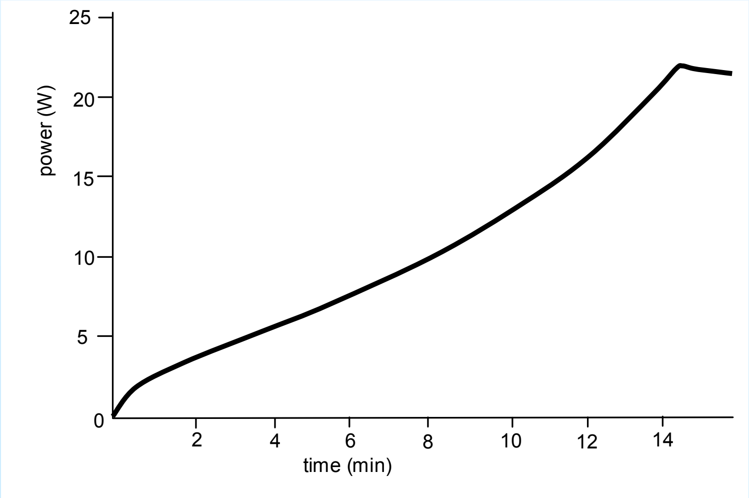


Cell parameters:

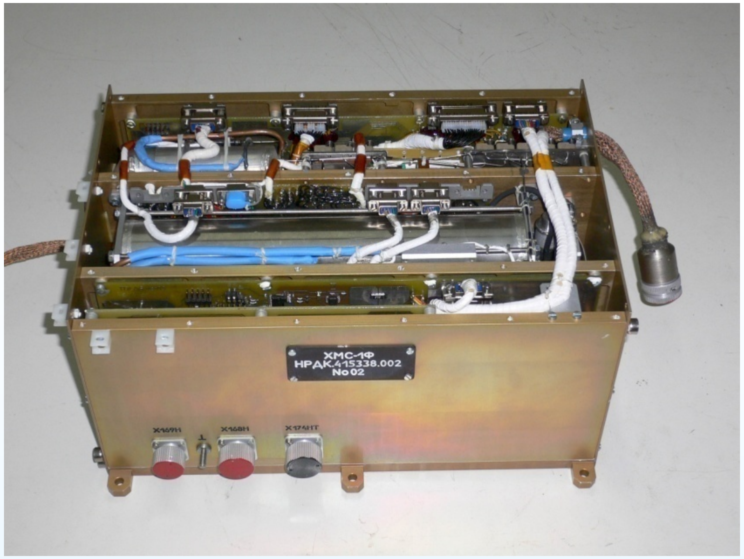
T max - 1000°C (1350°C)
W max - 22 W
Mass - 20 g

Test results





Gas Chromatograph



Tasks of the chromatograph

1. Accumulation of gases which are released from the sample during pyrolysis.

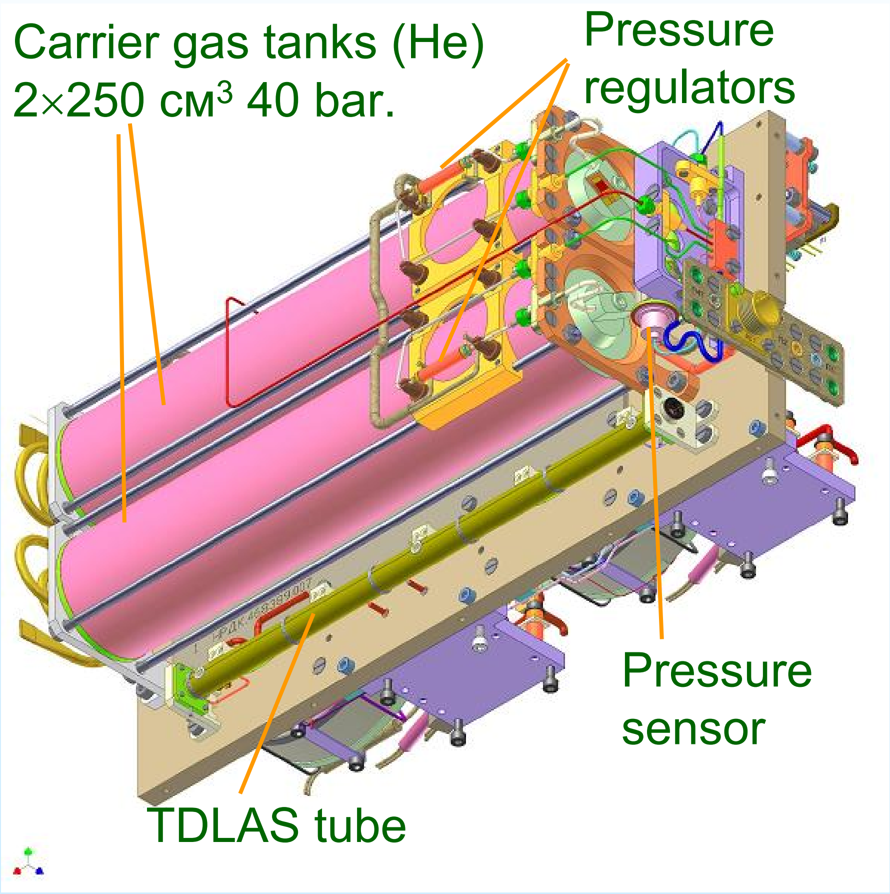
2. Redistribution of gases of different types (permanent gases, organics, etc.) between respective columns.

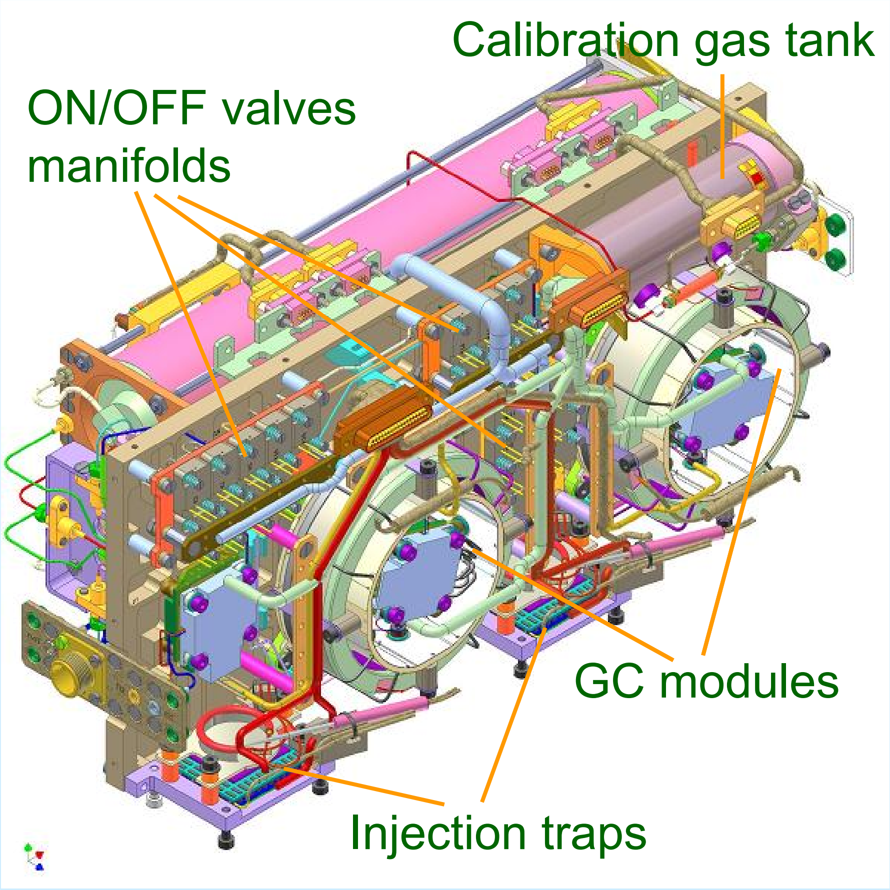
3. Separation of different gases by time of retention.

4. Measurement of abundance of separate gas component.

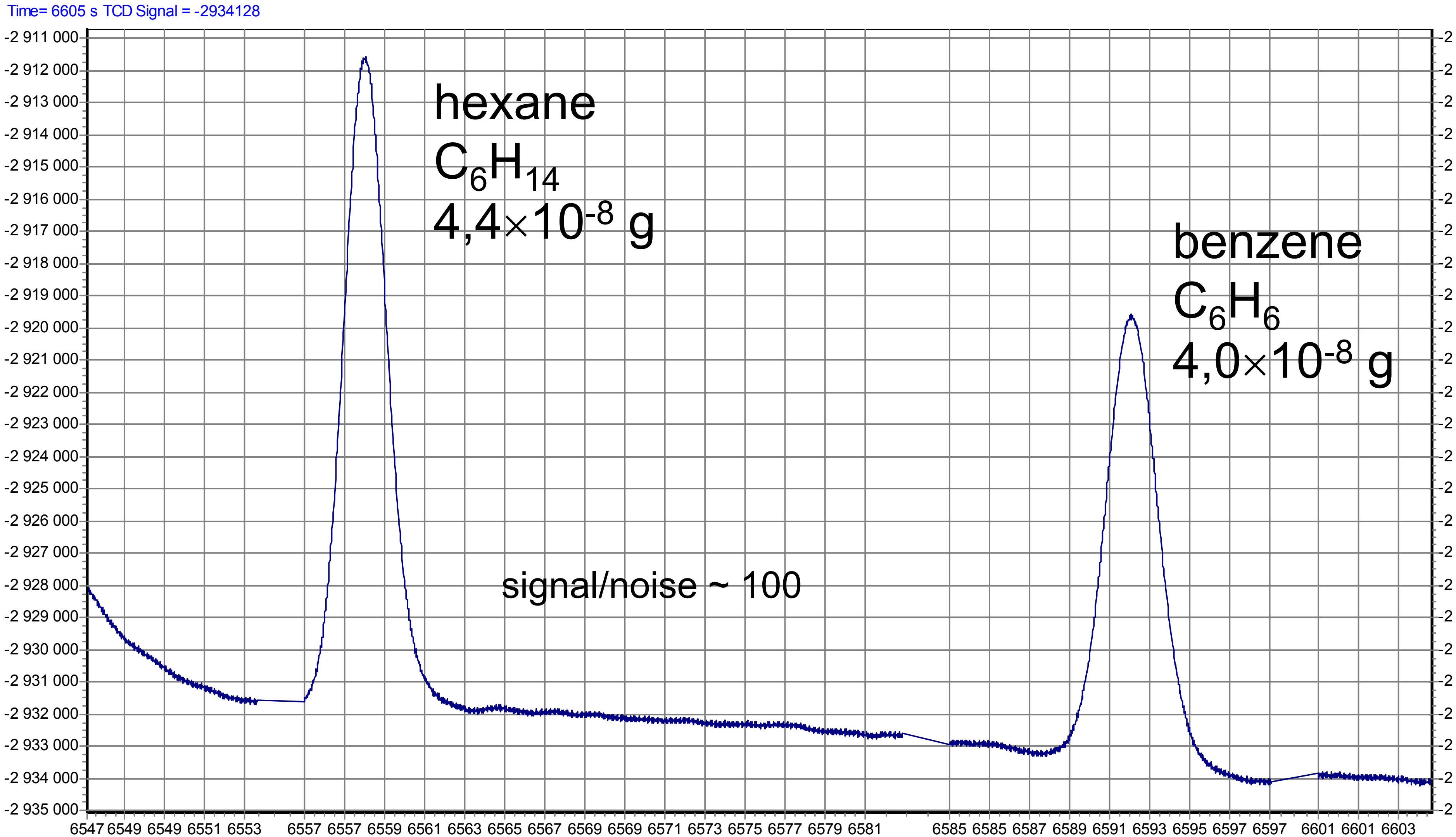
5. Measurement of isotopic ratios of D/H, $^{13}C/^{12}C$, $^{17}O/^{16}O$, $^{18}O/^{16}O$ in CO_2 and H_2O using TDLAS.

Assemblage of the GC block





A piece of test chromatogram



TDLAS scheme

Name*	Target molecule	Sigma (cm^{-1})	Lambda (nm)
C_2H_2	C_2H_2	6523.8794 cm^{-1}	1533 nm
CO_2iso	$^{18}OC^{16}O$	4898.7822 cm^{-1}	2041 nm
	$^{18}OC^{16}O$	4899.5653 cm^{-1}	
	$^{13}CO_2$	4899.6133 cm^{-1}	
H_2Oiso	HDO	3788.3366 cm^{-1}	2640 nm
	$H_2\,^{17}O$	3788.7852 cm^{-1}	
	$H_2\,^{18}O$	3788.9125 cm^{-1}	
H_2O-CO_2	H_2O	3727.7376 cm^{-1}	2682 nm
	CO_2	3728.4101 cm^{-1}	

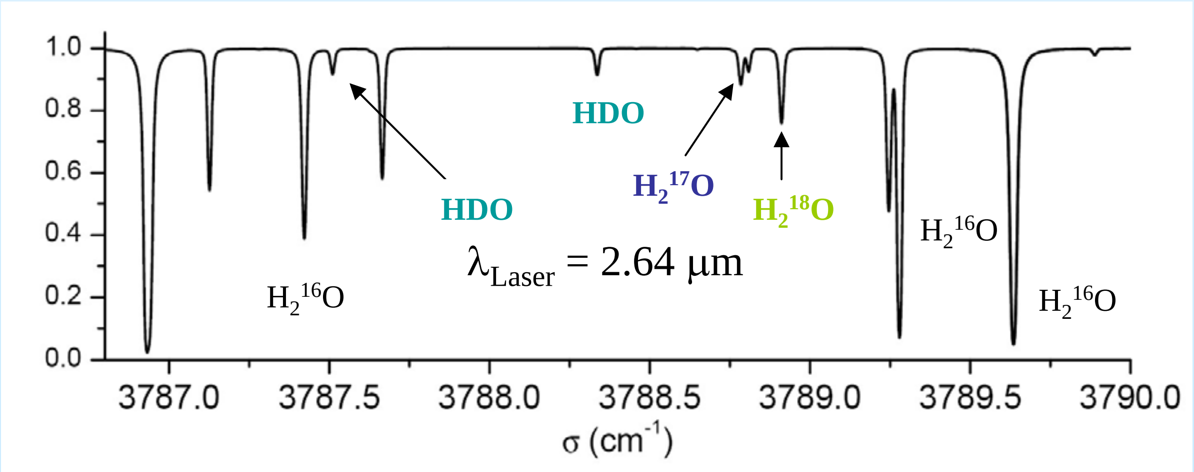
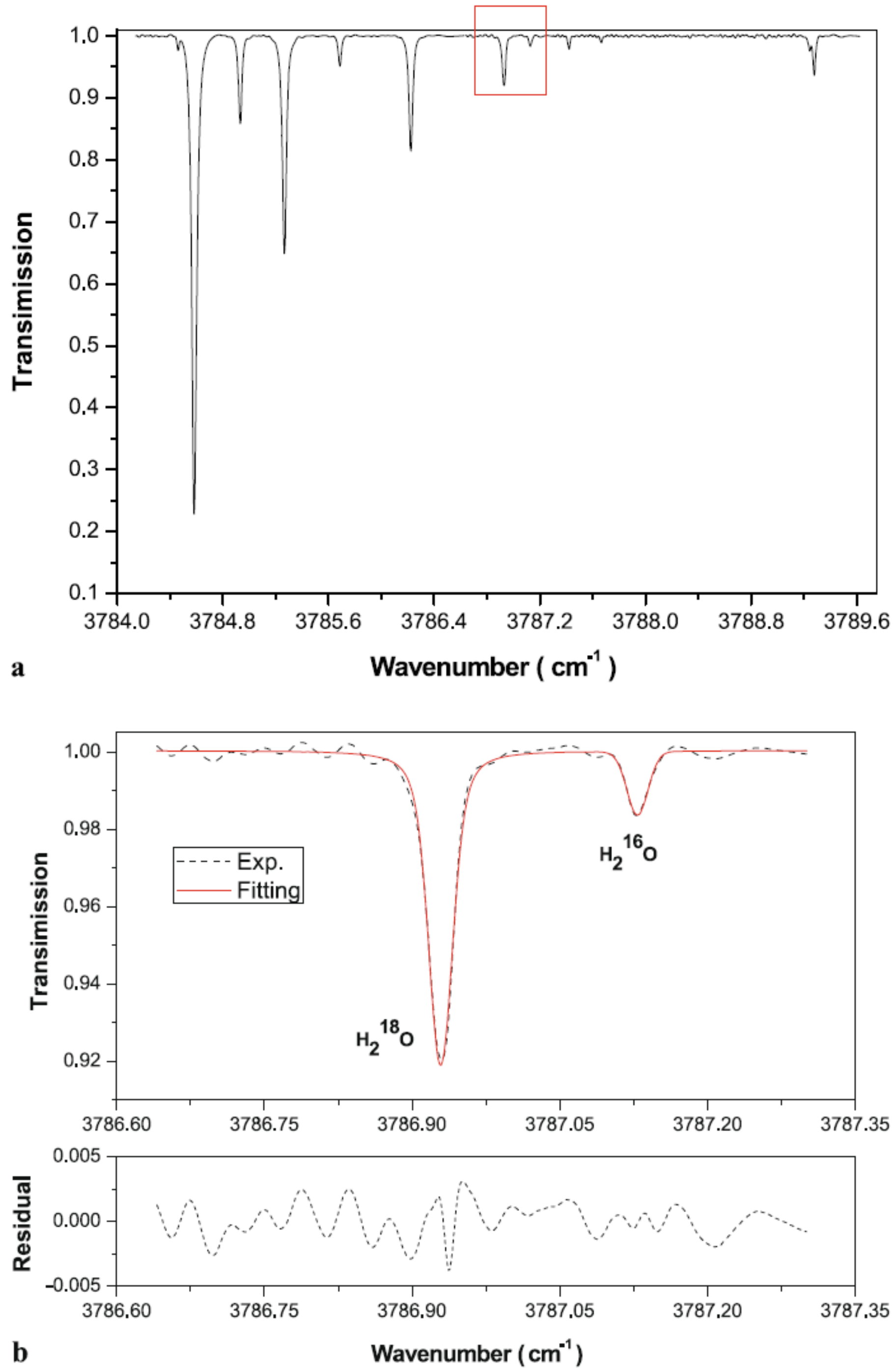
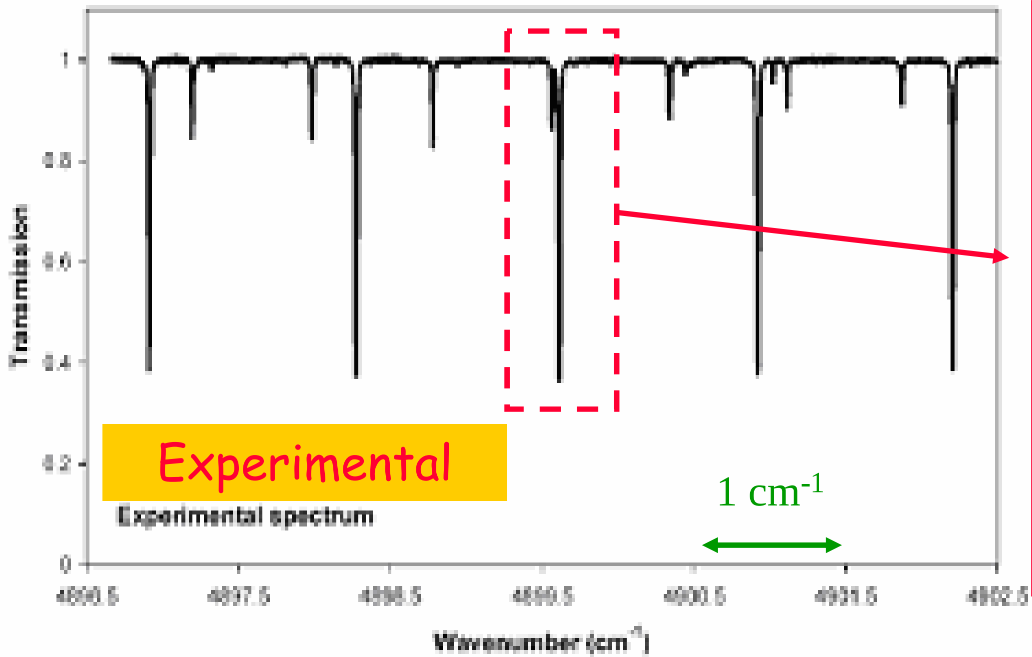
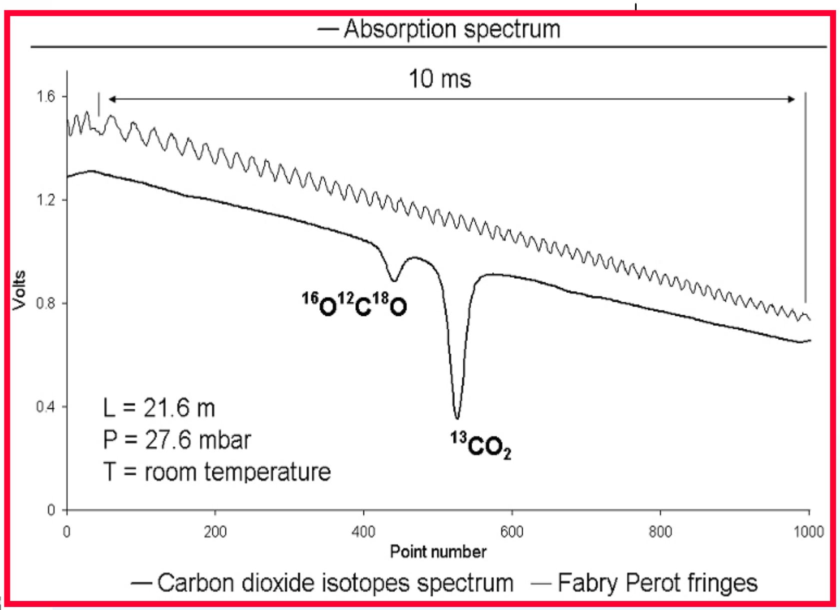


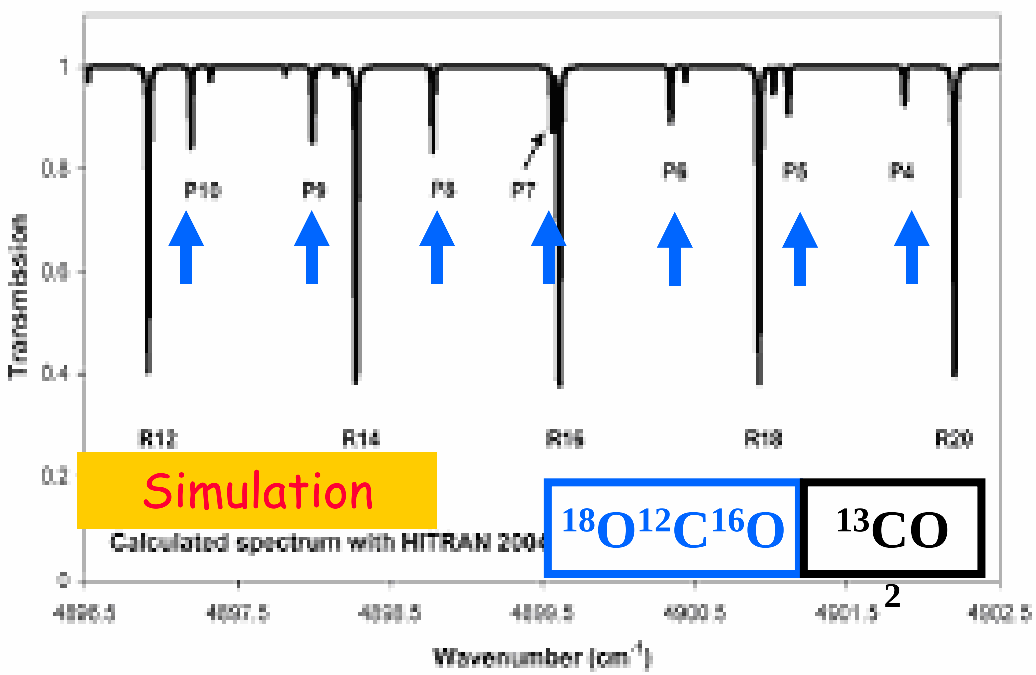
Fig. 6 (**a**) Example of H_2O spectrum achieved with the TDLAS laboratory model. A mixing of He and water vapor (10%) is injected in the capillary tube. The pressure is 218 hPa. (**b**) A zoom on some selected lines of $H_2{}^{18}O$ and $H_2{}^{16}O$ in (**a**). A simulated spectrum (in *red*) is superimposed to the experimental spectrum. Note that for this preliminary spectrum, the amount of water vapor was lower that what is expected during the analysis of the satellite soil and consequently we have fitted a $H_2{}^{18}O$ transition that is not in the spectroscopic study listed in this paper

[Durry et al., 2010]







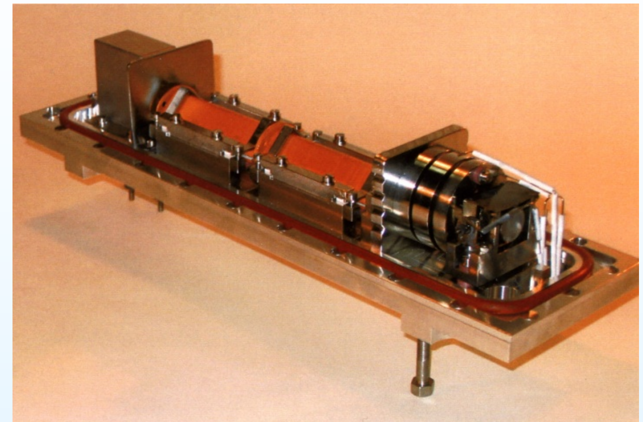


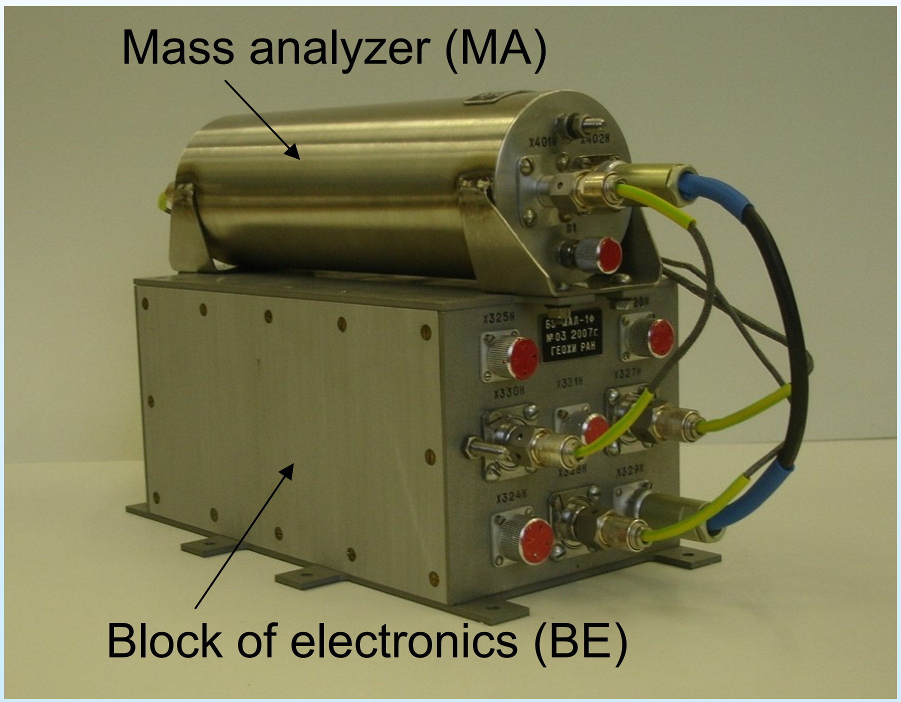
Laboratory experimental spectrum with Nanoplus Laser

$$\lambda_{Laser} = 2.04\ \mu m$$

The mass-spectrometer

L.P. Moskaleva (PI)
Vernadsky Institute of Geochemistry and Analytical Chemistry (GEOKHI)
Ryazan University (contractor)





Main parameters of the MS

1. Mass		- 3,5 кг
2. Power consumption		- 32 Вт
3. Dimentions:	MA	- 256x78x73 (mm)
	BE	- 256x110x120 (mm)
4. Mass range		- (2÷400) amu/q
5. Sensitivity for Ar		- (3÷5)x10^{-12} hPa
6. Dynamic range		- 10^4
7. Mass resolution		- 400

Main partners of the Gas Analytic Package team

IKI RAS (Russia)	TDA+GC
GEOKHI RAS (Russia)	MS
LATMOS (France)	GC+TDLAS
LISA University of Paris (France)	GC
MPS (Germany)	GC
Polytechnic University of Hong Kong (China)	SOPSYS (TDA)