

LA CHIMIE AU SERVICE DE LA RECHERCHE DE TRACES DE VIE SUR MARS



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Journées de Chimie X-ENS-ESPCI 2023
Chimie et Origines de la Vie

09-05-2023

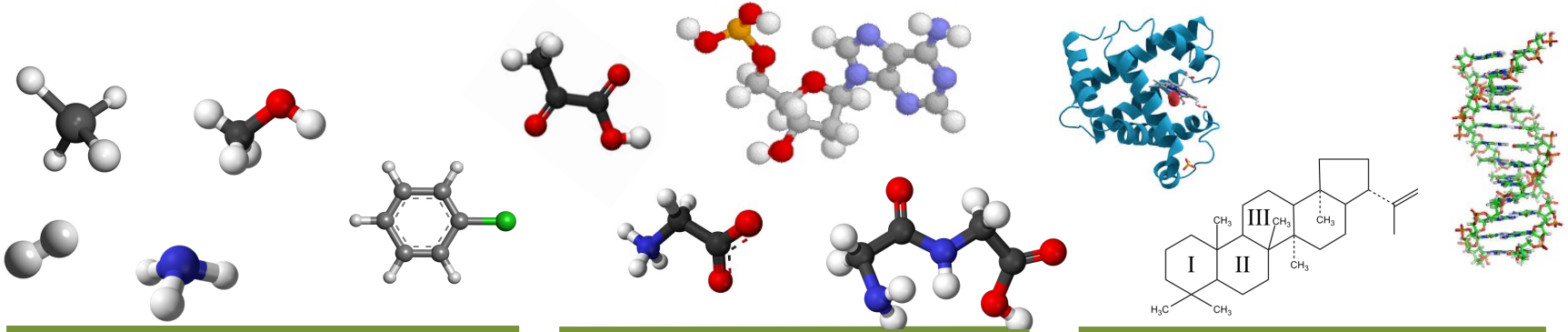


Terre

Chercher la vie extraterrestre
commence par comprendre l'apparition
et l'évolution de la vie sur Terre

PROBLÉMATIQUE COMMUNE : ORIGINE DE LA VIE ET MATIÈRE ORGANIQUE

L'astrochimie/exobiologie : étude des origines, de la distribution et de l'évolution des structures moléculaires et des processus liés à l'apparition de la vie



Molécules primordiales/simples

Molécules
prébiotiques

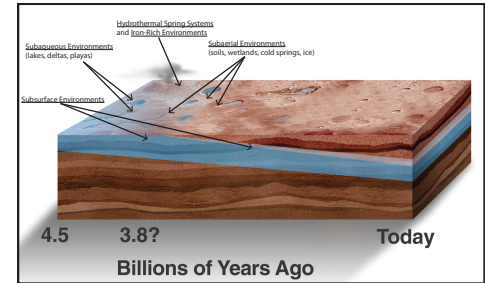
Molécules biologiques

Complexification chimique

Comment Rechercher la Vie Extraterrestre ?

→ Etudier le **contexte** général du lieu

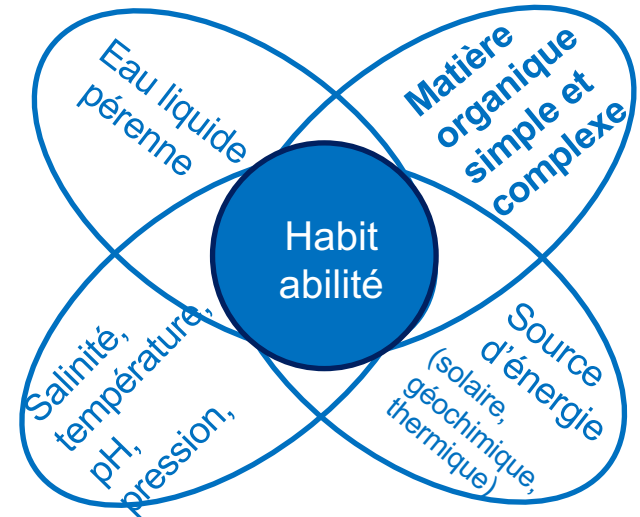
La géologie se prête-elle à la **préservation** des traces d'une vie passée ?
Le contexte est-il favorable à une étude *in situ* ?



→ Comprendre l'**habitabilité** globale et locale de là où l'on cherche

Les conditions étaient-elles réunies pour que la vie y apparaisse et/ou s'y pérennise ?

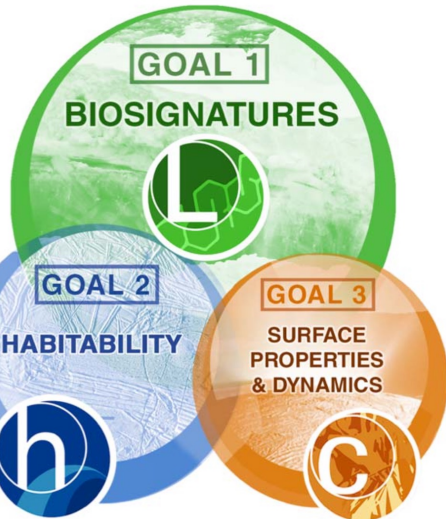
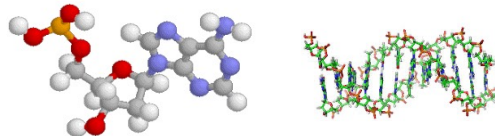
Environnement stable dans le temps



→ Rechercher des

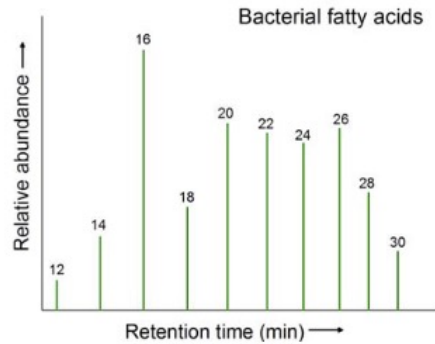
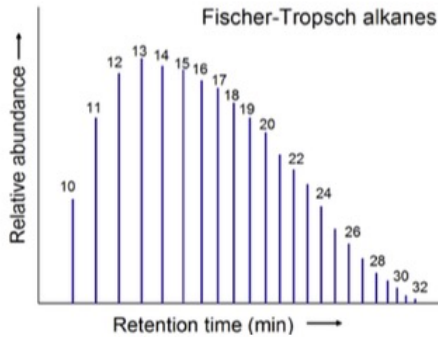
biosignatures/traces directes de vie

Y a-t-il ou y a-t-il eu de la vie à cet endroit? (matière organique complexe)

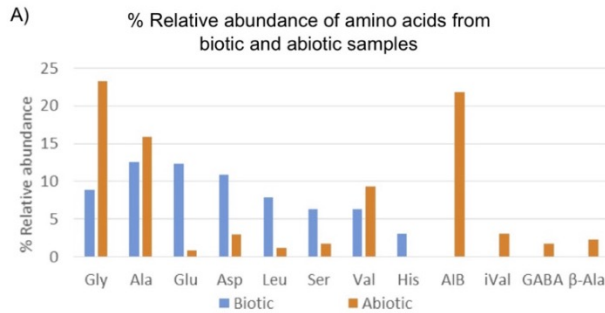


PROBLÉMATIQUE COMMUNE : ORIGINE DE LA VIE ET MATIÈRE ORGANIQUE

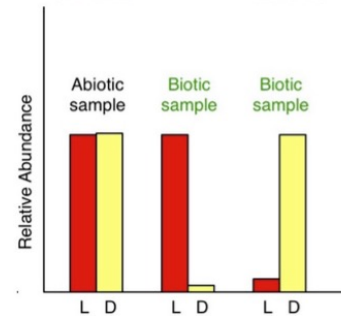
-> Recherche des biosignatures/traces directes de vie (Life)
 - Y a-t-il ou y a-t-il eu de la vie à cet endroit?



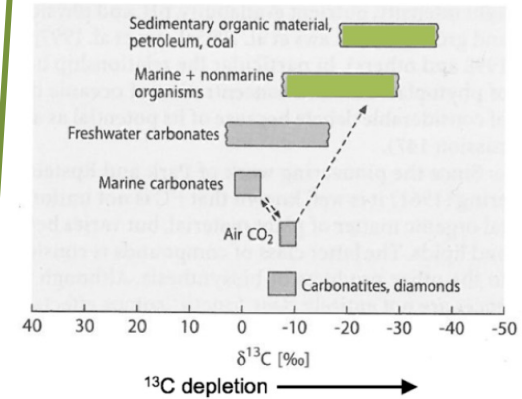
Distributions



Chiralité



Isotopes



ORGANIC DETECTION, CHARACTERIZATION, COMPOSITION

L-amino acid D-amino acid

ENANTIOMERIC EXCESS

carbon-13 carbon-12

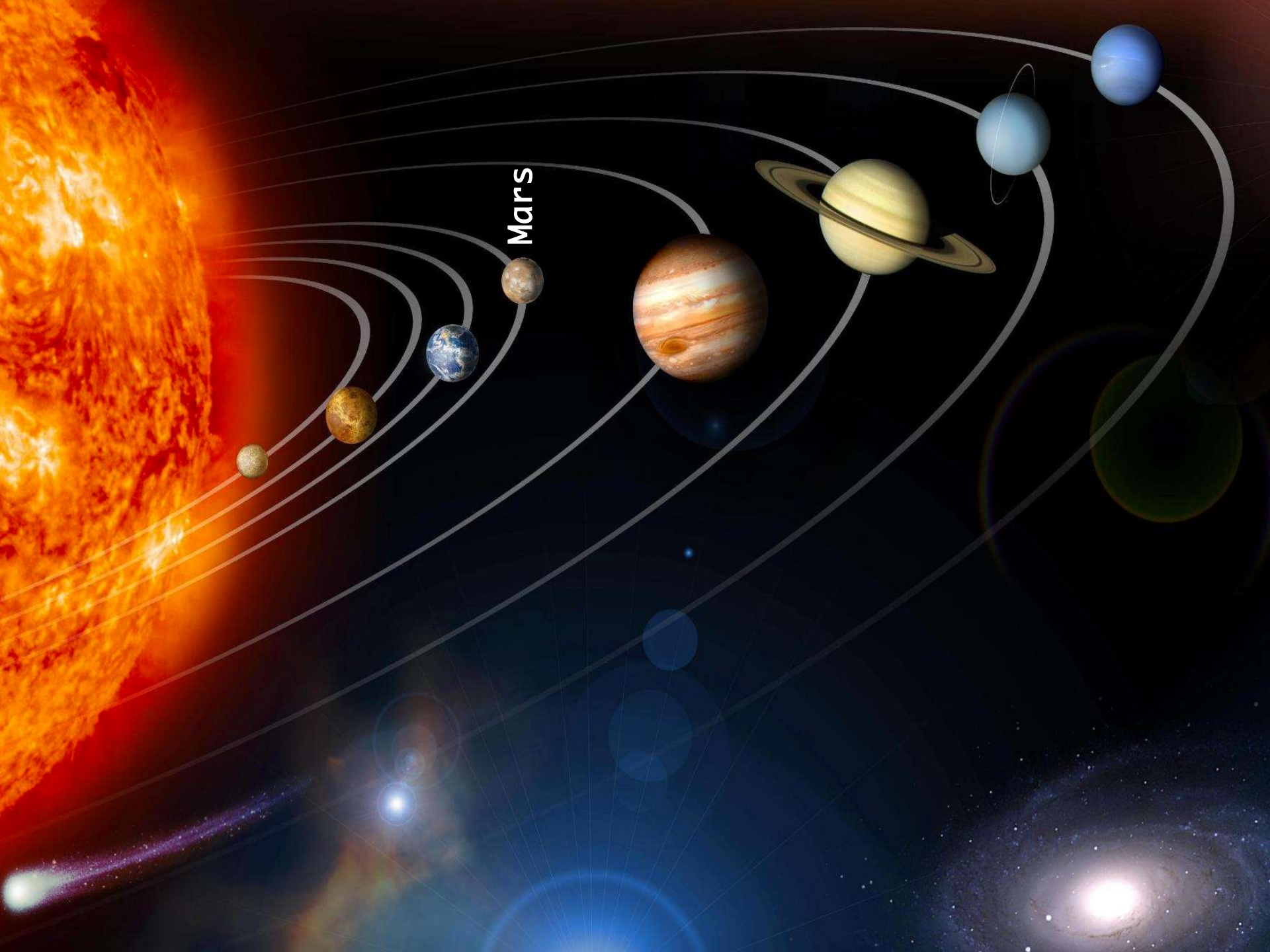
13 12

6 protons
7 neutrons
1.07% of all C
HEAVY

6 protons
6 neutrons
98.93% of all C
LIGHT

ISOTOPIC INDICATORS





Mars



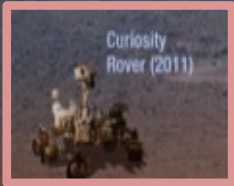
LET'S GO TO MARS!!

Aujourd'hui

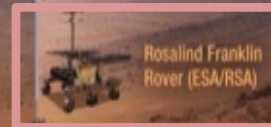
Demain



Eau + Habitabilité



Vie



Follow the Water

Explore Habitability

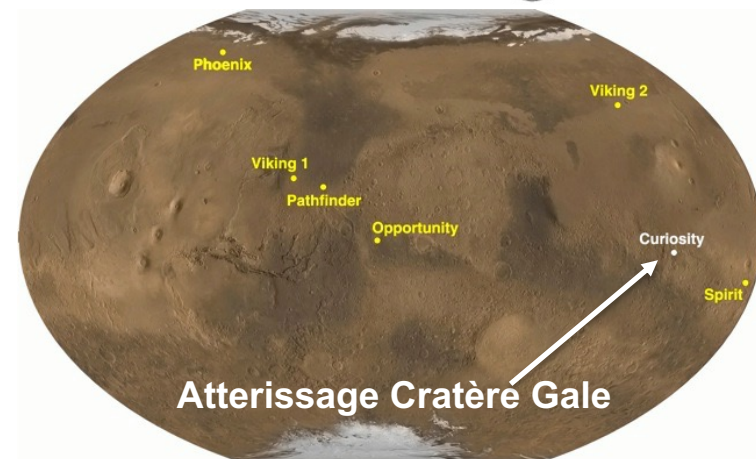
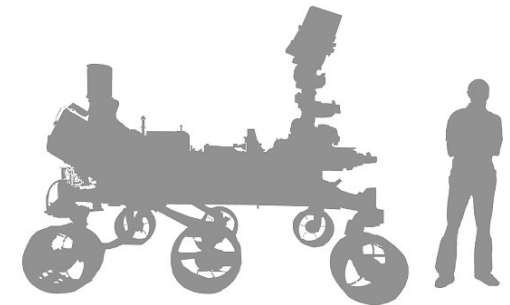
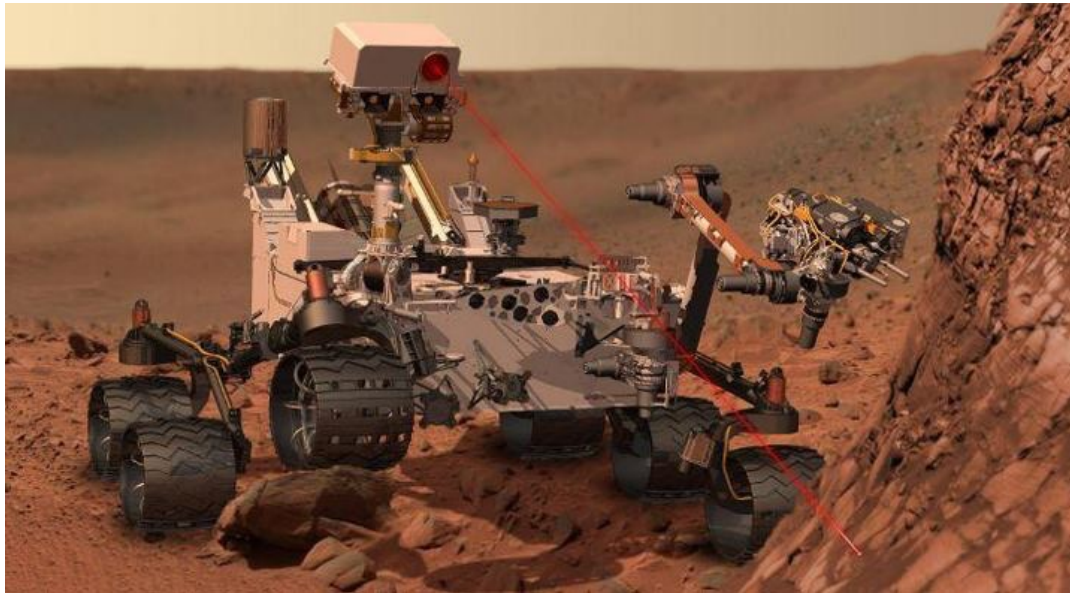
Seek Signs of Life

Prepare for Future Human Explorers

MARS SCIENCE LABORATORY

Curiosity, une collaboration internationale
(USA, France, Canada, Allemagne, Russie et Espagne)

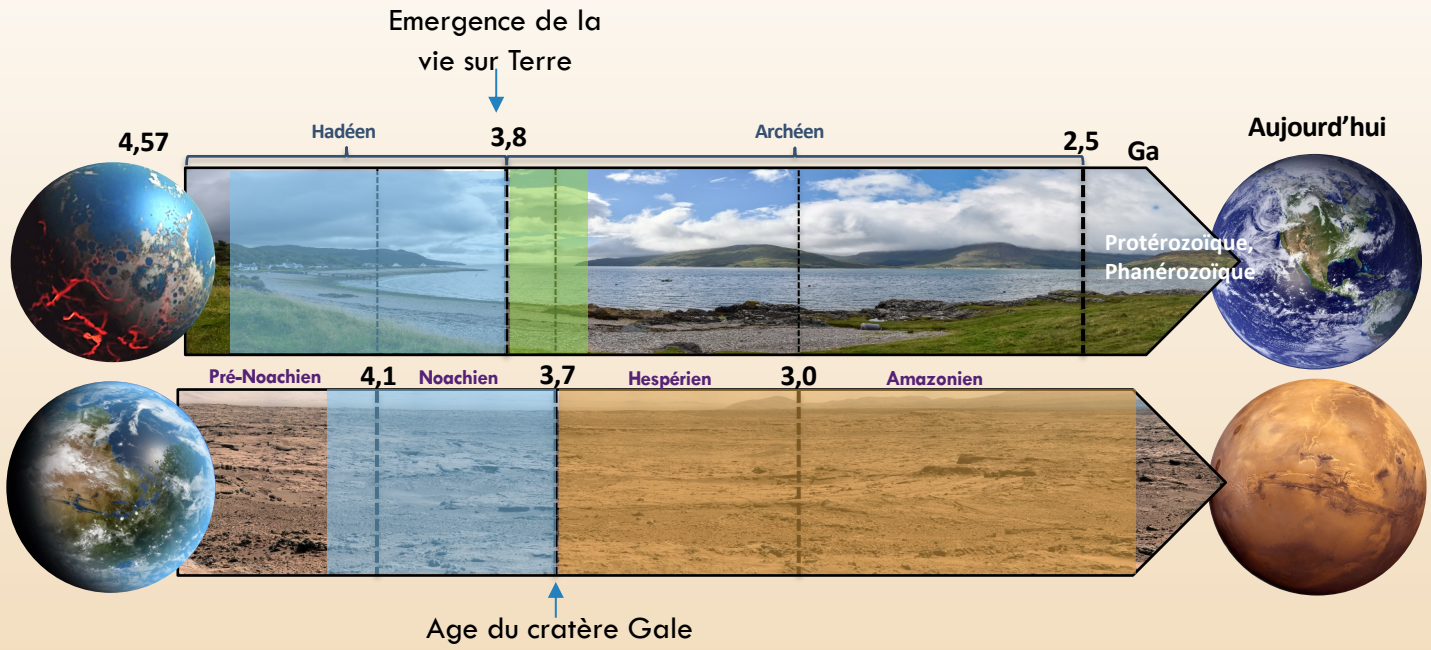
-> objectif: déterminer l'habitabilité de Mars



- Longueur 3 m, largeur 2,7 m, masse 900 kg dont 80 kg d'instruments scientifiques
- Lancement novembre 2011 de Cape Canaveral, Floride.
- Touchdown sur Mars Août 2012 – Cratère Gale (proche équateur)



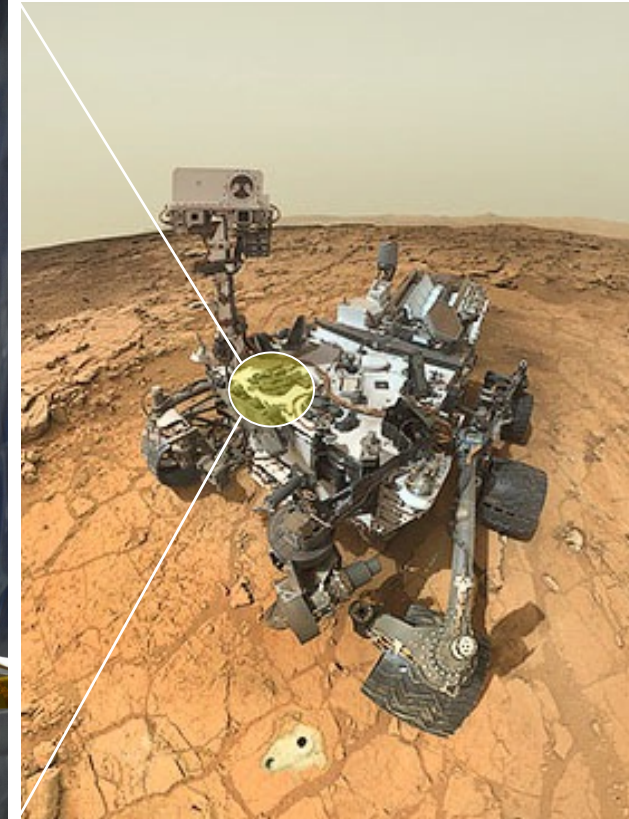
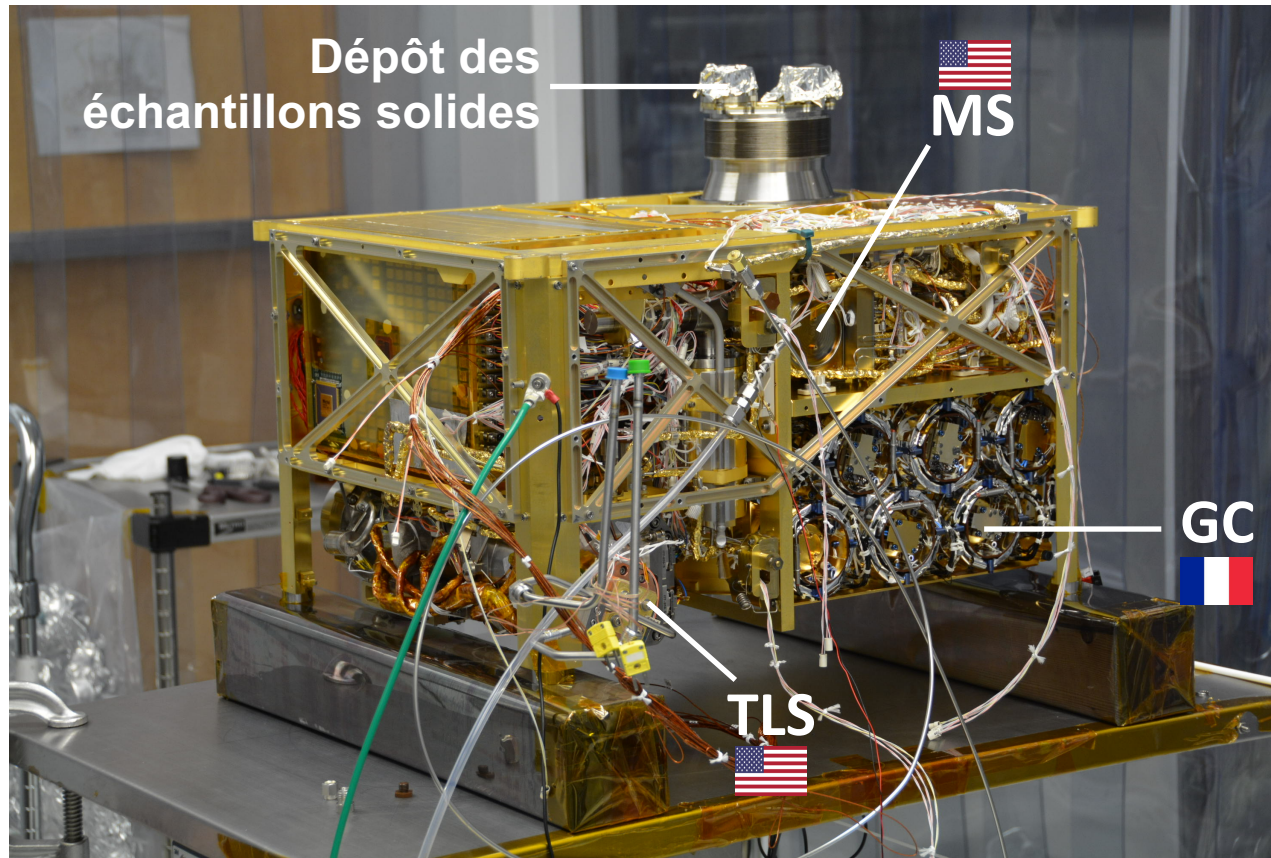
**POUR
TROUVER UN
MONDE PLUS
ACCUEILLANT...
REMONTONS
LE TEMPS**



Conditions environnementales passées similaires entre Mars et la Terre
(Mojziz et al., 1996 & 2001; Schopf et al., 2002; Westall et al., 2005 & 2015)

<p>Eau liquide pérenne <i>(Bibring et al. 2006, Carter et al. 2010)</i></p>	<p>Sources énergétiques : Soleil, sources hydrothermales ?</p>	<p>Molécules organiques essentielles à la vie</p>
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Mars propice au développement d'une chimie prébiotique voire du vivant



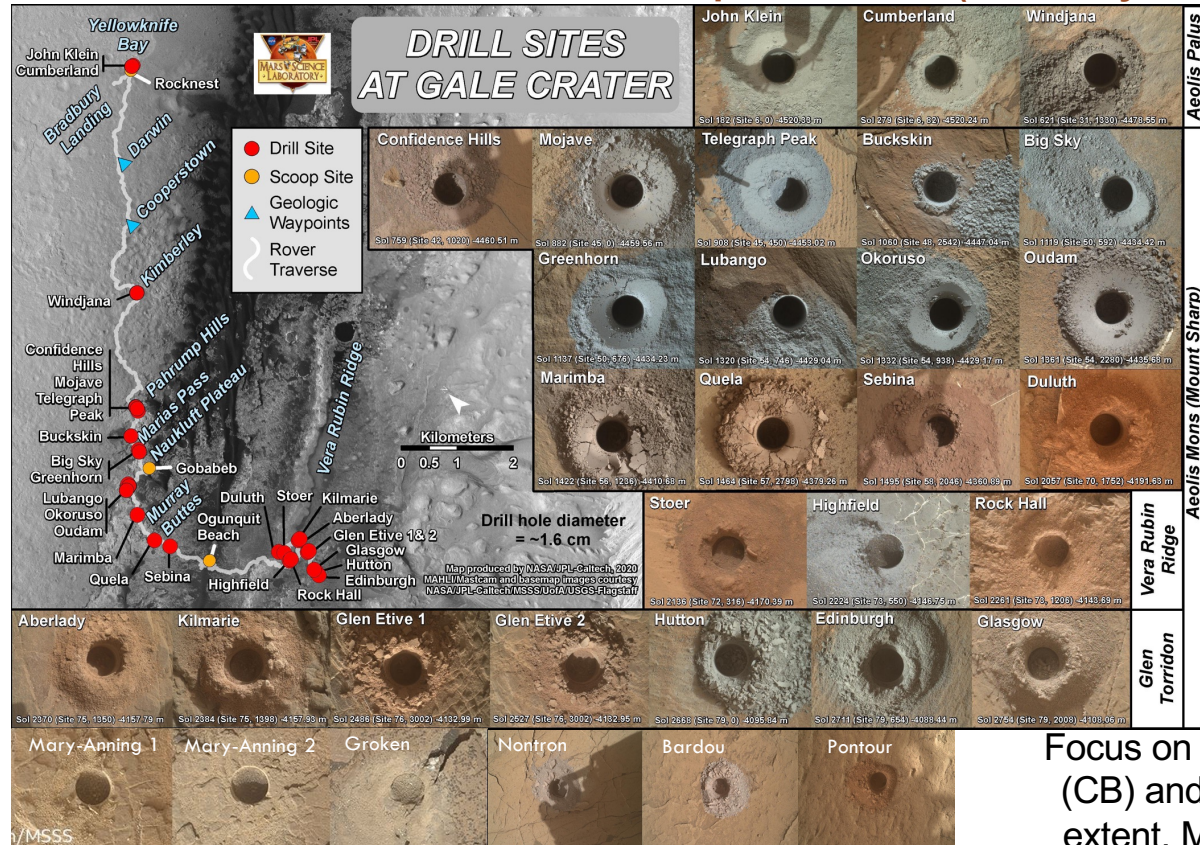
Chromatographe Gazeux (GC) – Sépare les composés d'un mélange de molécules
Spectromètre de Masse (MS) – Identifie les molécules par leur masse moléculaire
Spectromètre Laser (TLS) – Méthane et Isotopes

MSL DE 2011 À AUJOURD'HUI



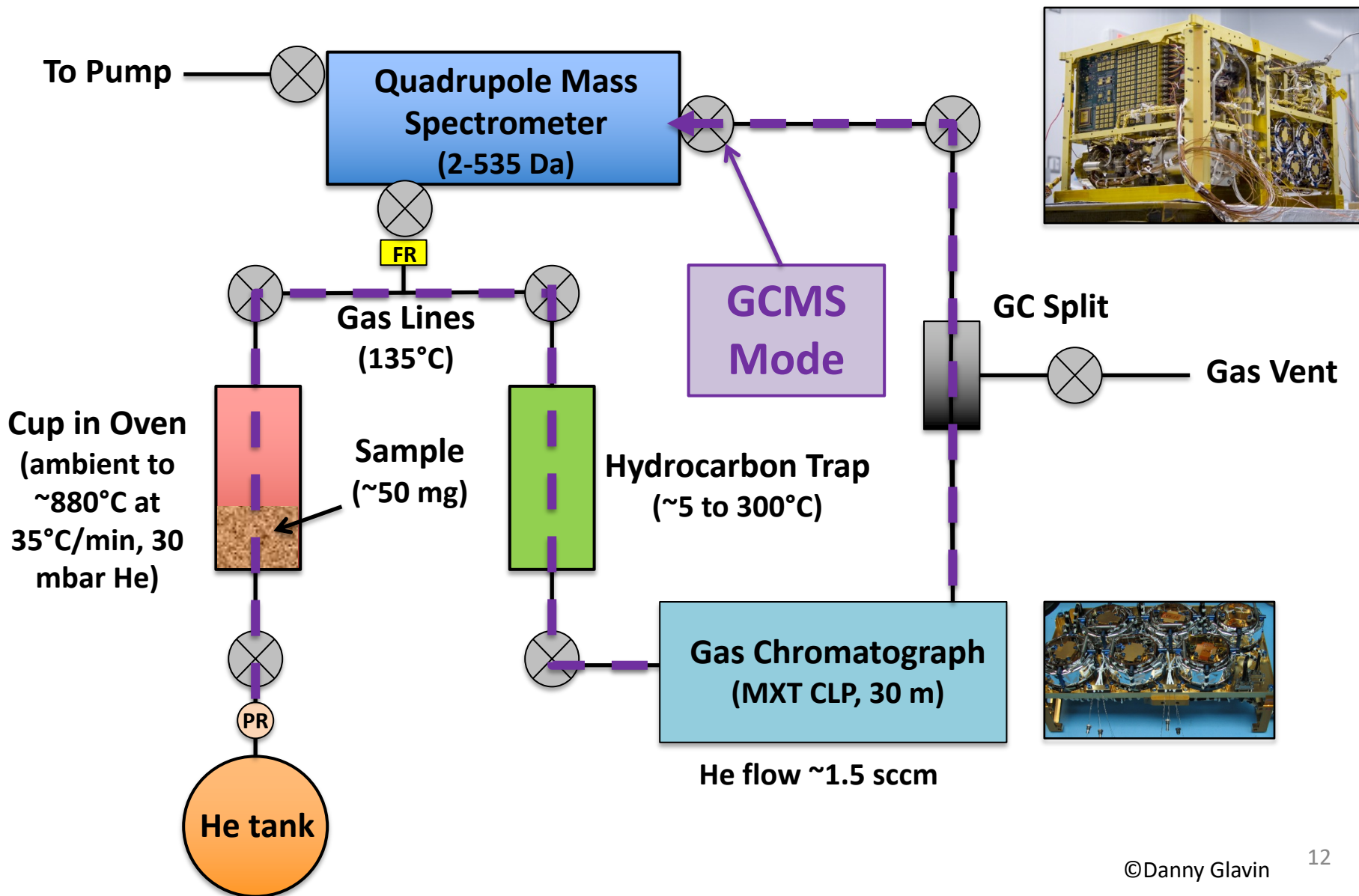
Curiosity since 2012:

- > 3300 active sols (10th anniversary in Aug)
- 29 km driven, 610 m elevation
- 36 drilled samples (30 analyzed with SAM)
- 3 scooped locations (all 3 analyzed with SAM)

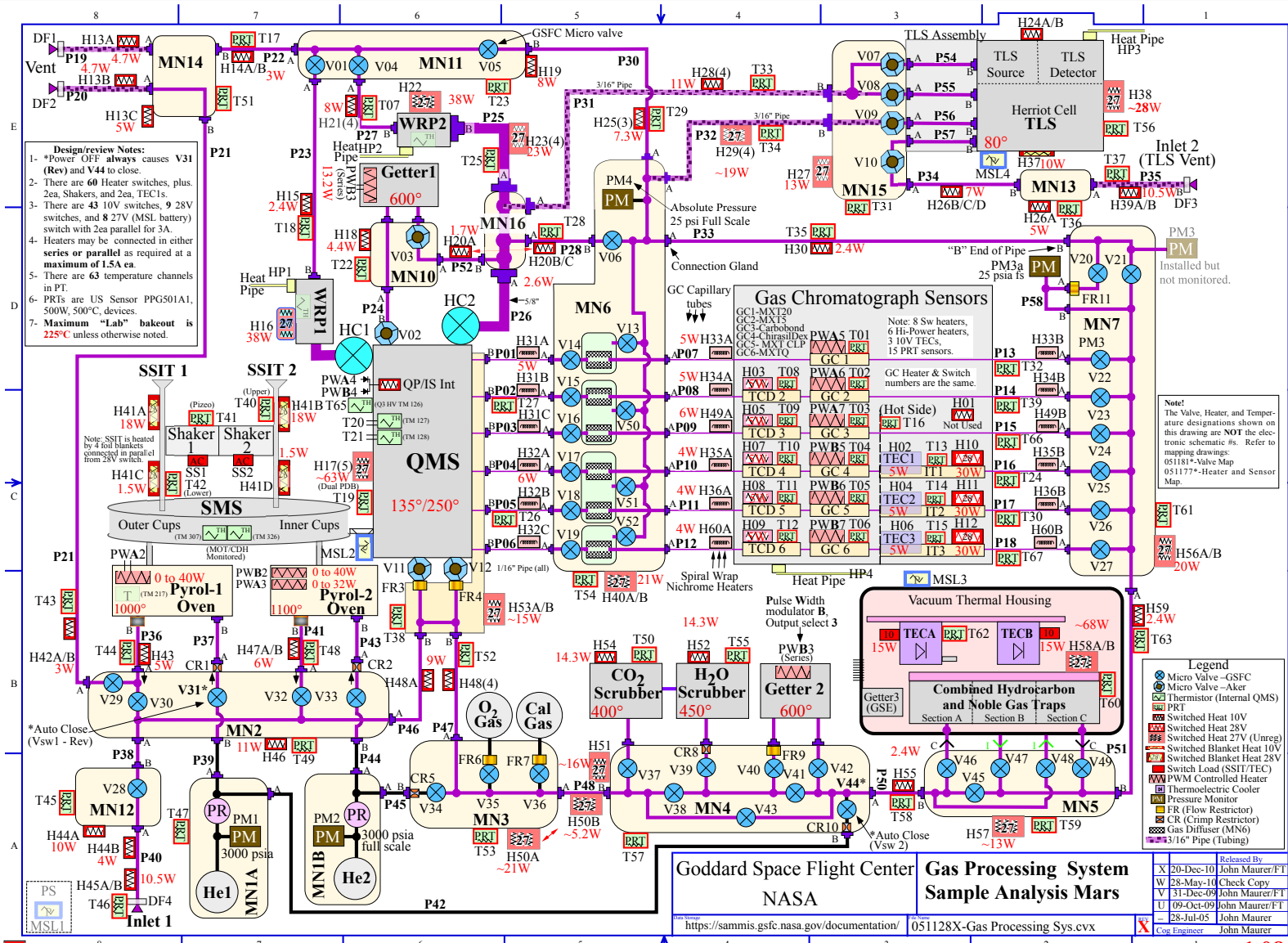


Focus on Cumberland (CB) and to a lesser extent, Mojave (MJ)

Simplified SAM Gas Flow Diagram



VERSION NON-SIMPLIFIÉE...



Design/Review Notes:

- 1- "Power" OFF always causes V31 (Rev) and V44 to close.
- 2- There are 60 Heater switches, plus 2ea, Shakers, and 2ea, TEC1s.
- 3- There are 43 10V switches, 9 28V switches, and 8 27V (MSL battery) switch with 2ea parallel for 3A.
- 4- Heaters may be connected in either series or parallel as required at a maximum of 1.5A ea.
- 5- There are 63 temperature channels in PT.
- 6- PRTs are US Sensor PPG501A1, 500W, 500°C, devices.
- 7- Maximum "Lab" bakeout is 225°C unless otherwise noted.

Note: SSIT is heated by 4 foil blankets connected in parallel from 28V switch.

Note: The Valve, Heater, and Temperature designations shown on this drawing are NOT the electronic schematic #s. Refer to mapping drawings: 051181* Valve Map 051177* Heater and Sensor Map

- Legend**
- Micro Valve - GSFC
 - Micro Valve - Aker
 - Thermistor (Internal QMS)
 - PRT
 - Switched Heat 10V
 - Switched Heat 28V
 - Switched Heat 27V (Unreg)
 - Switched Blanket Heat 10V
 - Switched Blanket Heat 28V
 - Switch Load (SSIT/TEC)
 - PWM Controlled Heater
 - Thermoelectric Cooler
 - Pressure Monitor
 - FR (Flow Restrictor)
 - CR (Crimp Restrictor)
 - Gas Diffuser (MN6)
 - 3/16" Pipe (Tubing)

Goddard Space Flight Center
NASA

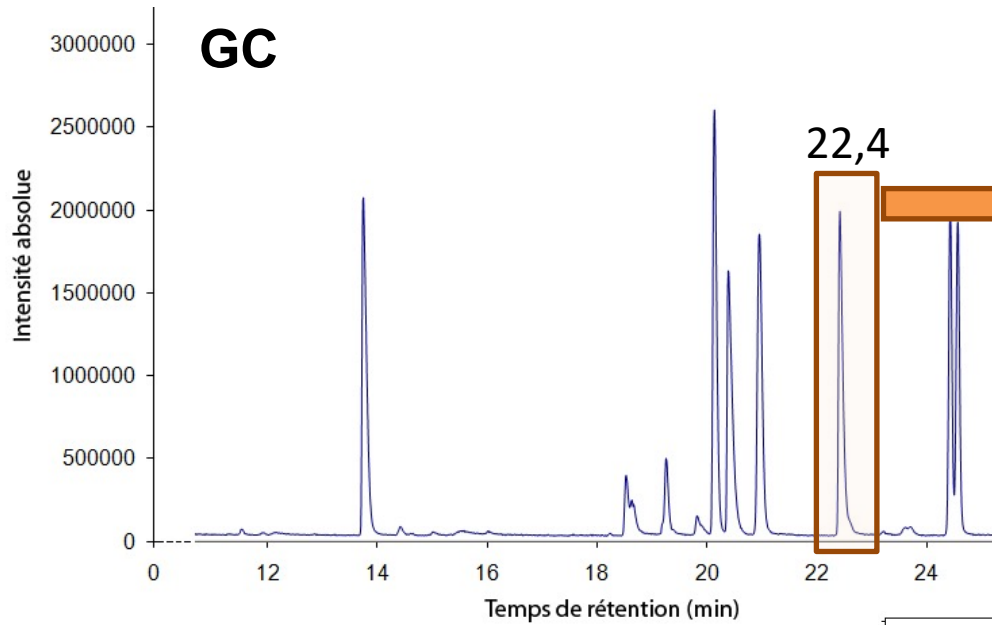
Gas Processing System
Sample Analysis Mars

Released By:	J. Maurer/FT
X 20-Dec-10	John Maurer/FT
W 28-May-10	Check Copy
V 31-Dec-09	John Maurer/FT
U 09-Oct-09	John Maurer/FT
28-Jul-05	John Maurer
Cog Engineer	John Maurer

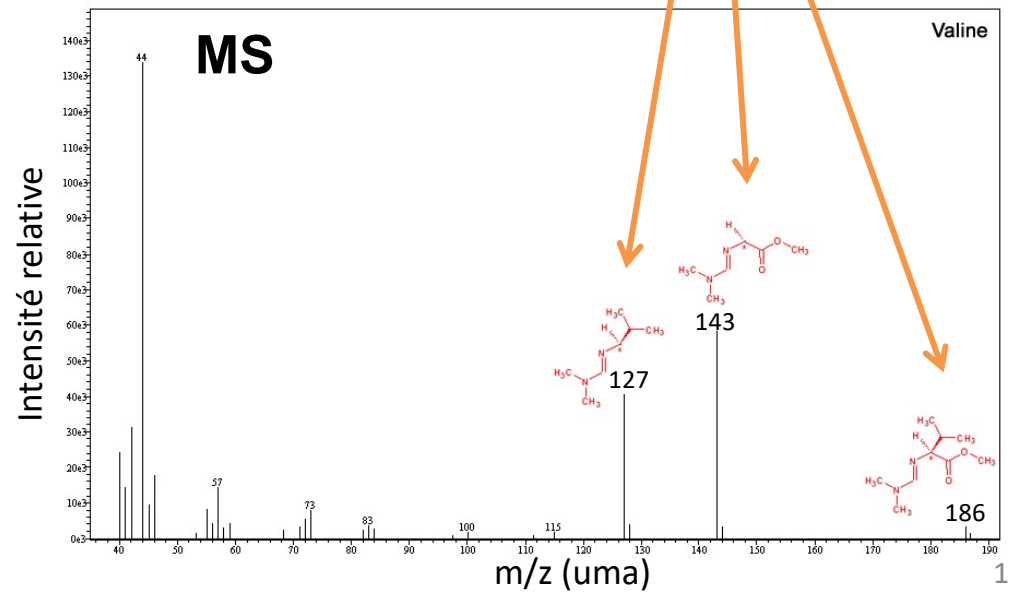
<https://samms.gsfc.nasa.gov/documentation/>

051128X-Gas Processing Sys.cvx

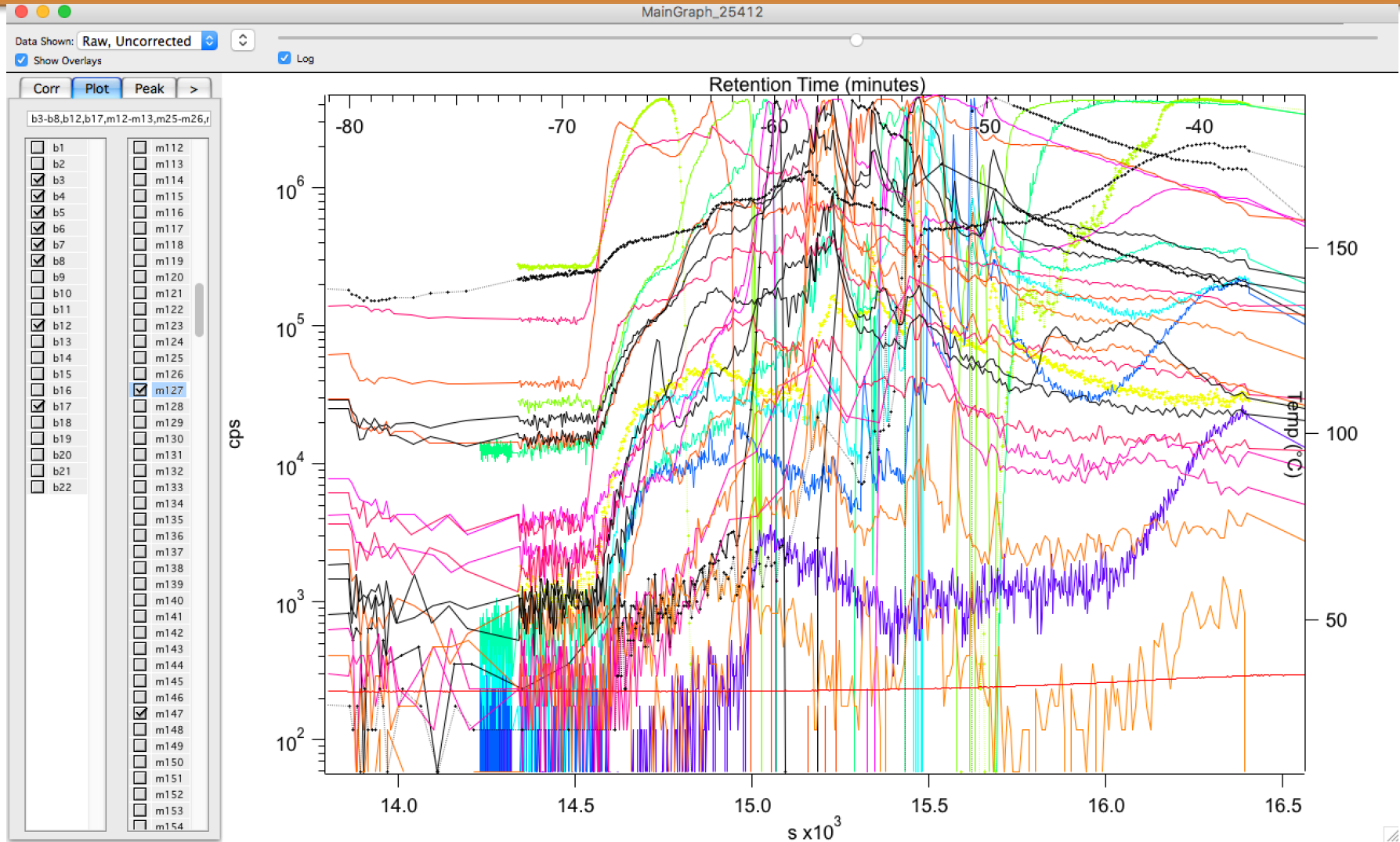
IDENTIFICATION DES MOLÉCULES DÉTECTÉES



Fragmentation
(reproductible)

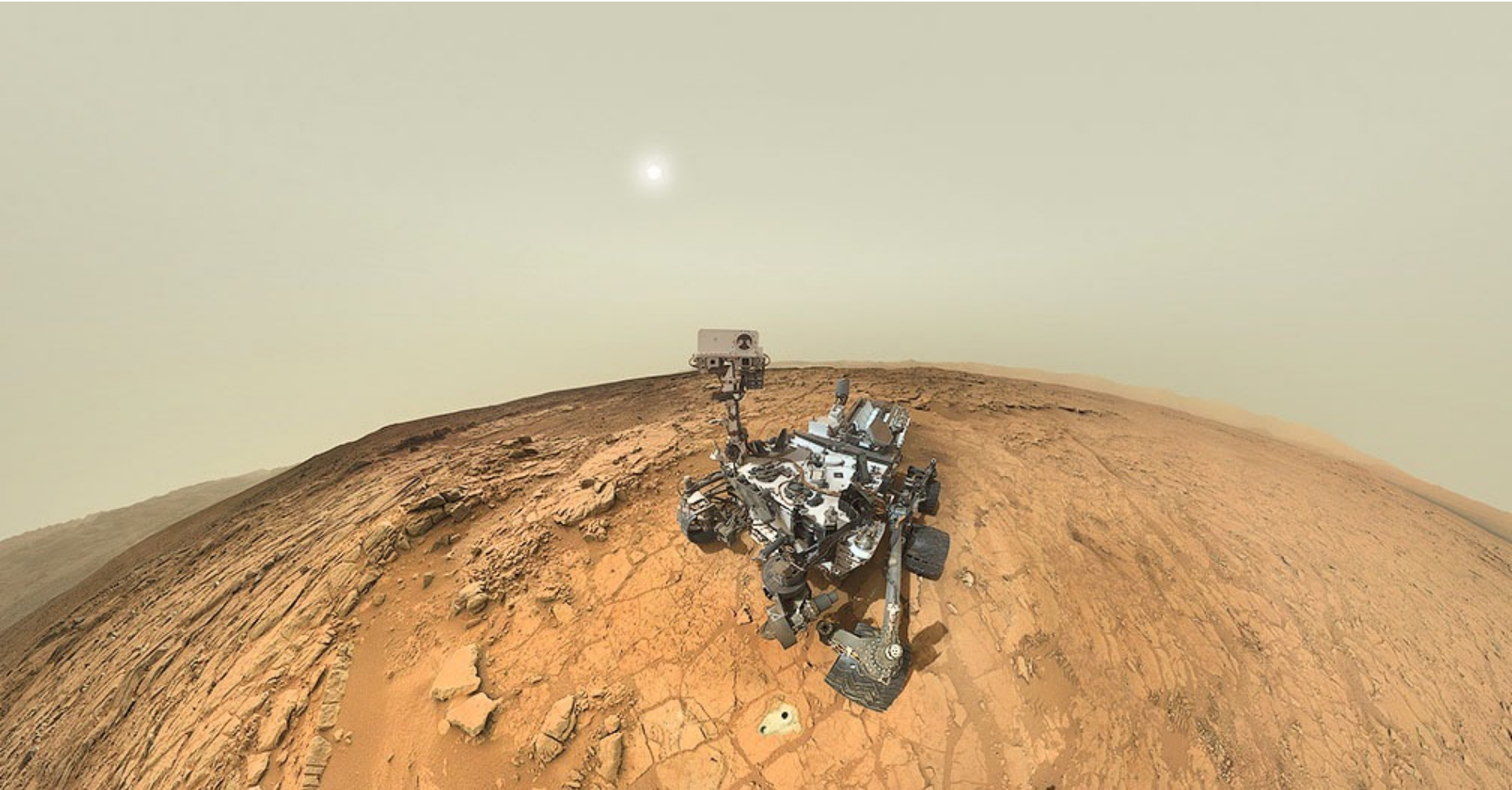


EN VRAI, A QUOI RESSEMBLENT NOS DONNÉES BRUTES



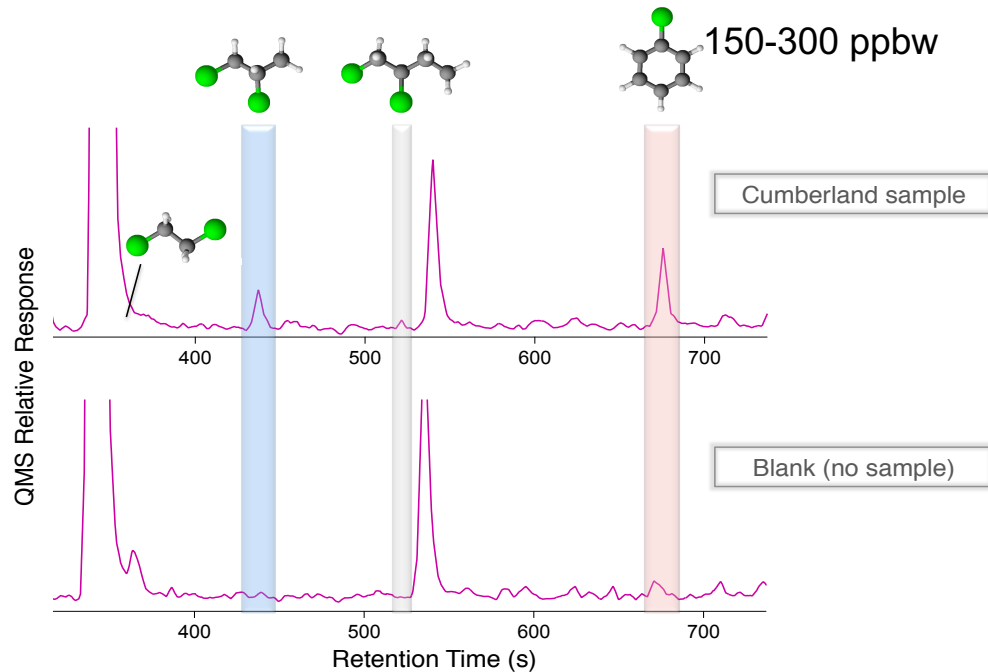
- Processus d'analyse long et complexe
- Nécessité d'une recherche dirigée

FOCUS SUR CUMBERLAND (CB)

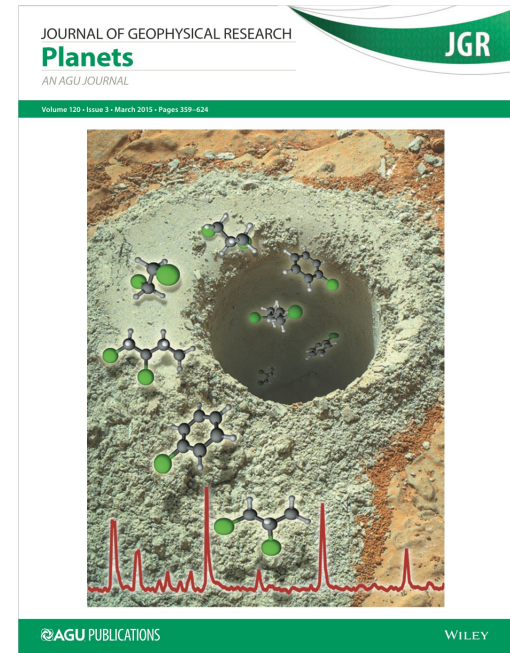


Yellowknife Bay:
Gale crater floor sediment
Lake deposit

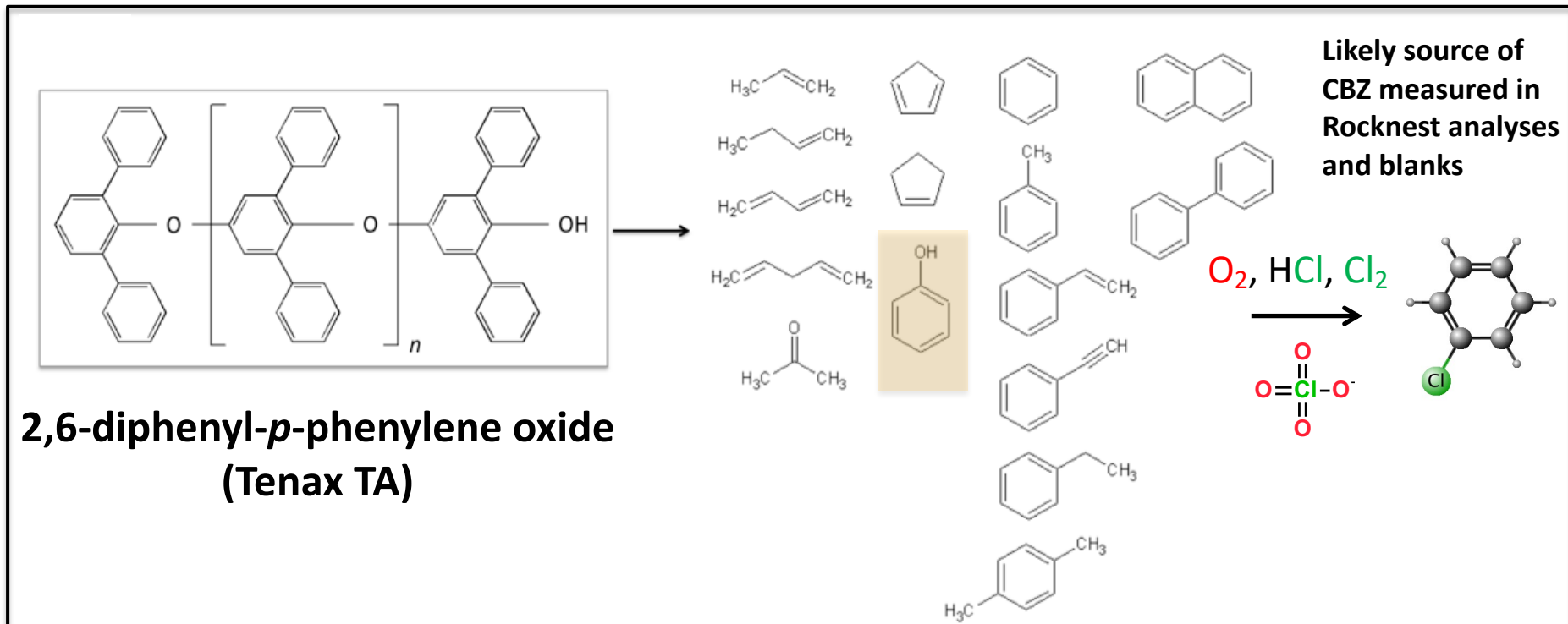
PREMIÈRE DÉCOUVERTE DE MOLÉCULES ORGANIQUES SUR MARS!



Première détection de molécules organiques martiennes (GCMS – SAM)*



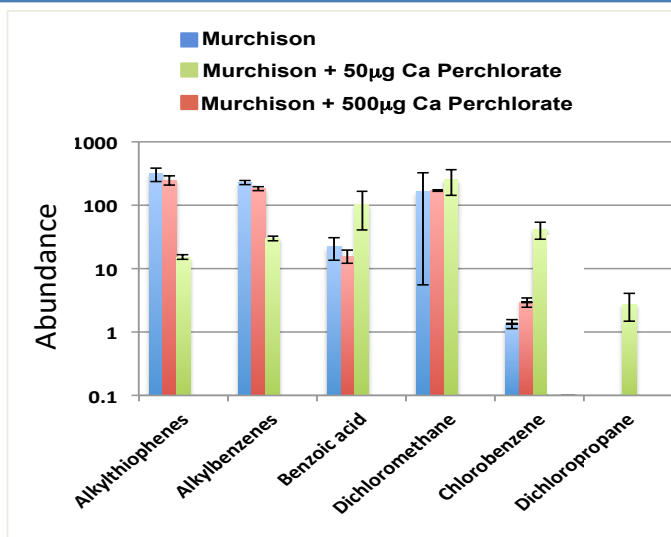
MAIS D'OÙ VIENT LE CBZ PRÉSENT DANS LE BRUIT DE FOND DE CHAQUE ÉCHANTILLON ?



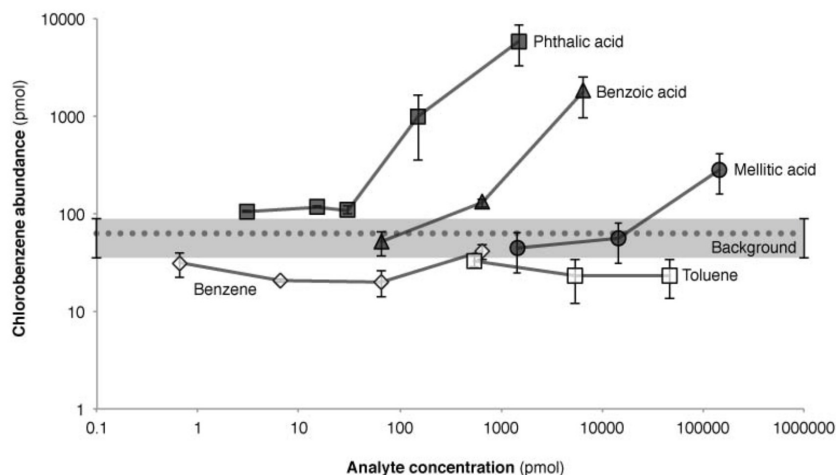
**2,6-diphenyl-*p*-phenylene oxide
(Tenax TA)**

- > Le Tenax subit une dégradation chimique et thermique résultant en une variété de molécules aromatiques et aliphatiques.
- > Le benzène relargué du piège n'est probablement pas une source de C pour le chlorobenzène observé. (Miller *et al.*)
- > Le phénol relargué du piège est la source probable du C dans le chlorobenzène du **bruit de fond** observé en laboratoire et sur SAM.

À LA RECHERCHE DE L'ORIGINE DU CBZ DÉTECTÉ



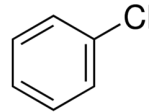
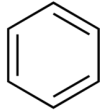
Du chlorobenzene est produit lors de la pyrolyse de l'extrait organique de la météorite de Murchison en présence de perchlorate de calcium (Miller).



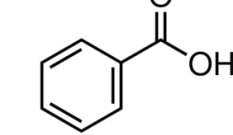
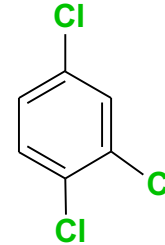
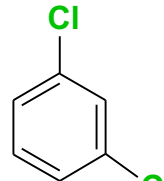
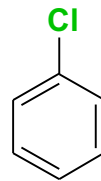
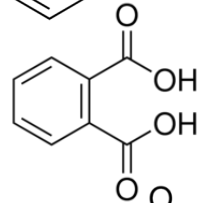
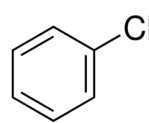
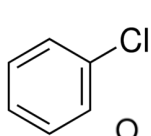
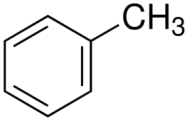
Les expériences de labo montrent une production de cbz lors de la pyrolyse d'aromatiques **fonctionnalisés** (e.g. acide phthalique) en présence de Ca- ou Mg-perchlorate (Miller-Martin).

À LA RECHERCHE DE L'ORIGINE DU CHLOROBENZÈNE DÉTECTÉ SUR MARS

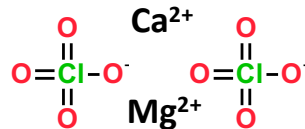
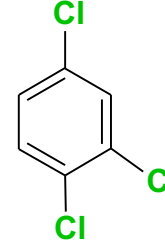
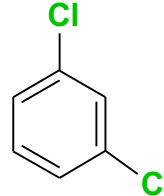
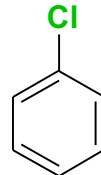
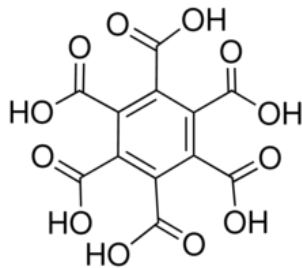
0.65 nmol
benzene



47 nmol
toluene



>15 nmol
mellitic
acid



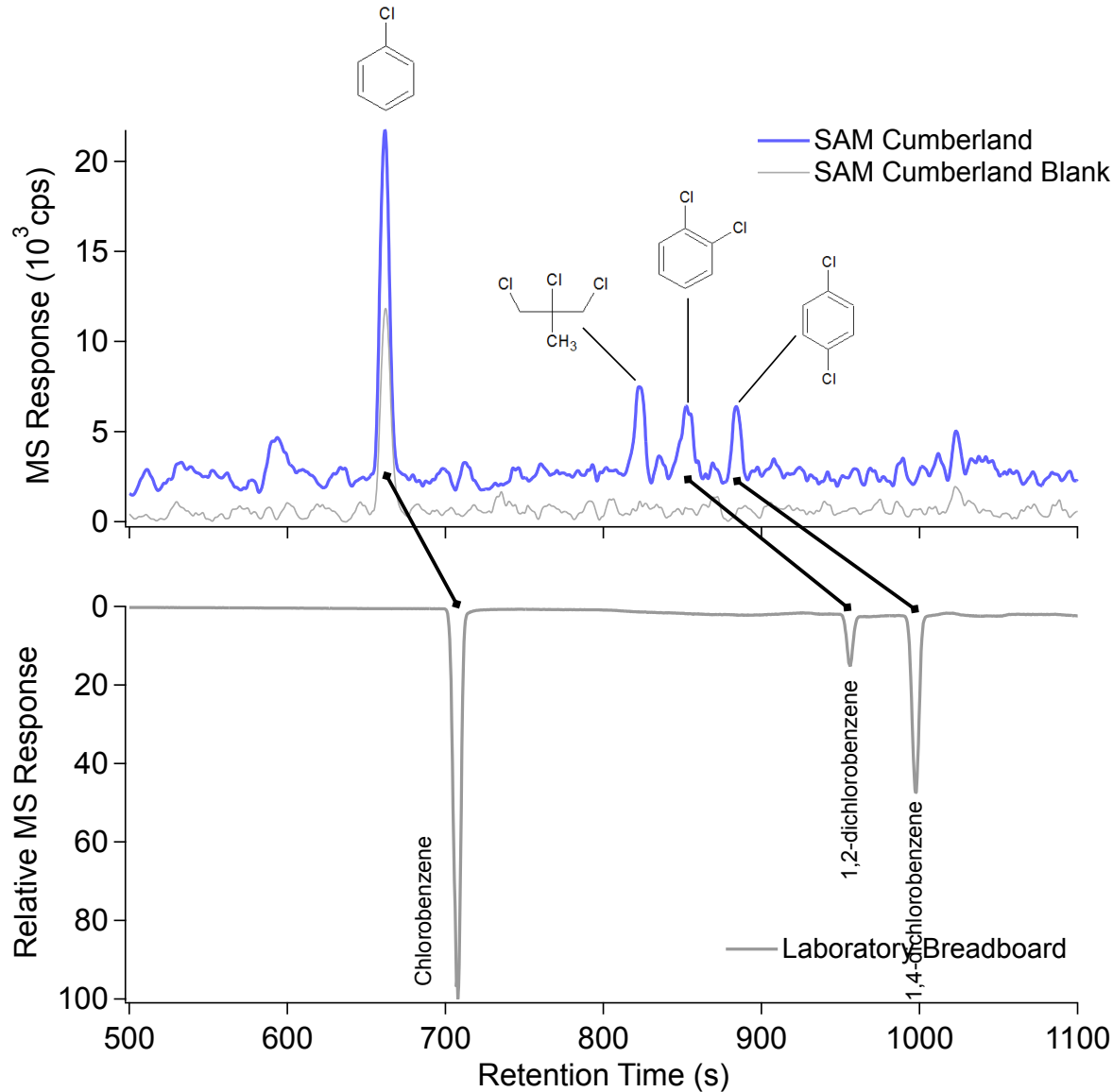
T > 200°C

Chlorine/HCl released from the CaPC replaces more electronegative functional groups, like OH, but does not easily substitute for H or methyl groups.



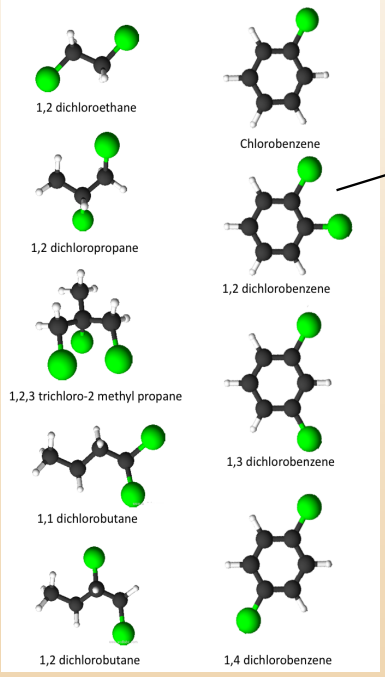
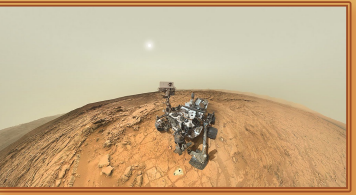
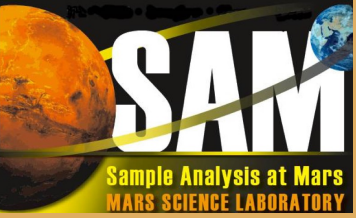
Instruments commerciaux

LA RÉ-ANALYSE DES DONNÉES DE CB

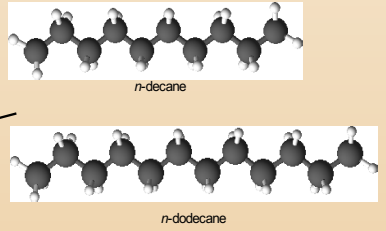
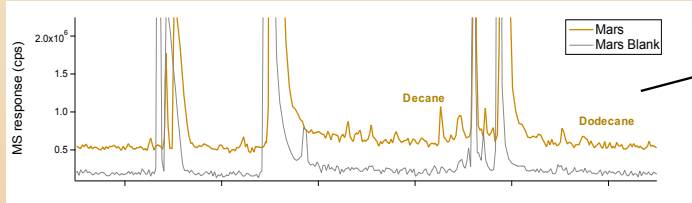
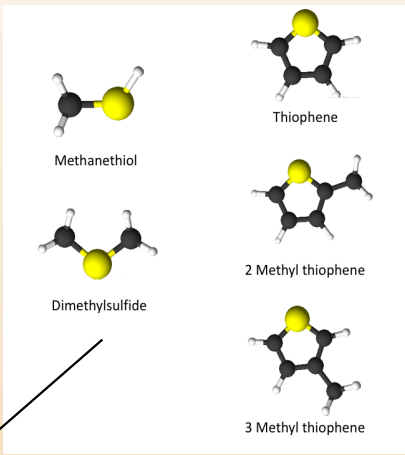
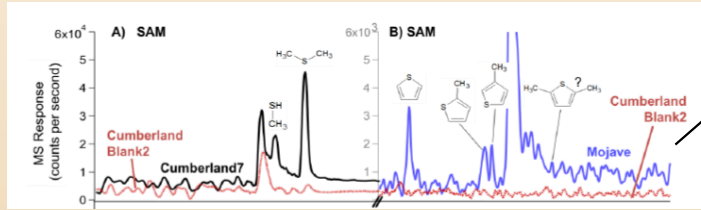
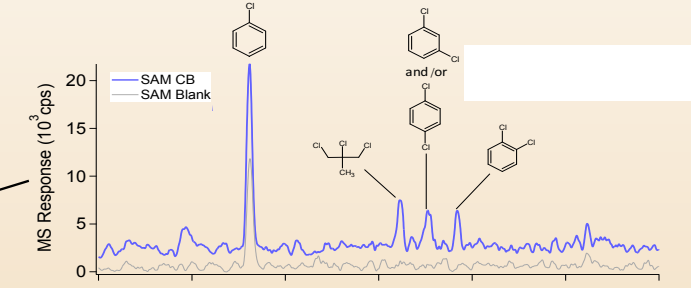


Un état de chlorination supplémentaire du benzène a été détecté dans le même échantillon CB (Szopa *et al.*).

Les données sont confirmées par les études de labo (Millan *et al.*).



$T_{\text{sample}} < 500^{\circ}\text{C}$



$T_{\text{sample}} > 500^{\circ}\text{C}$

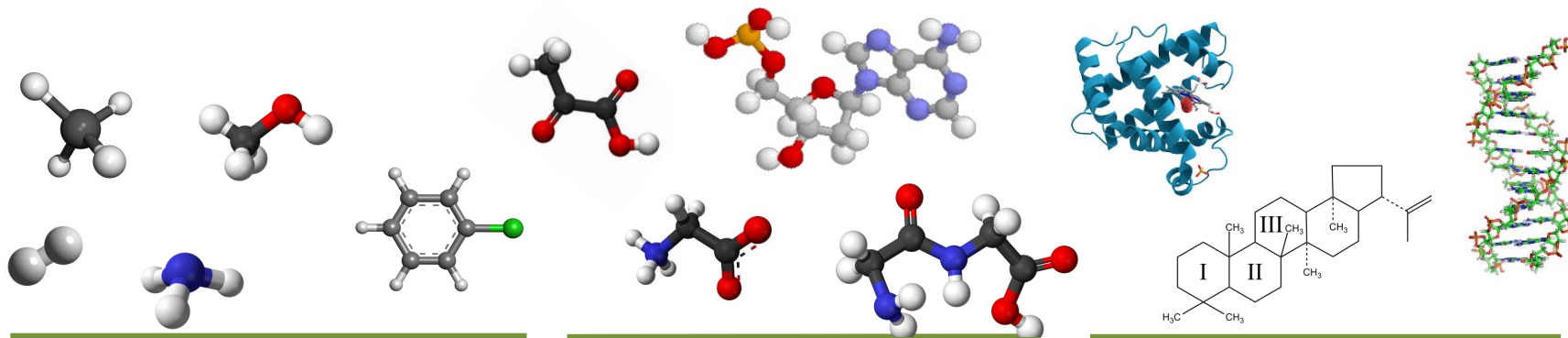
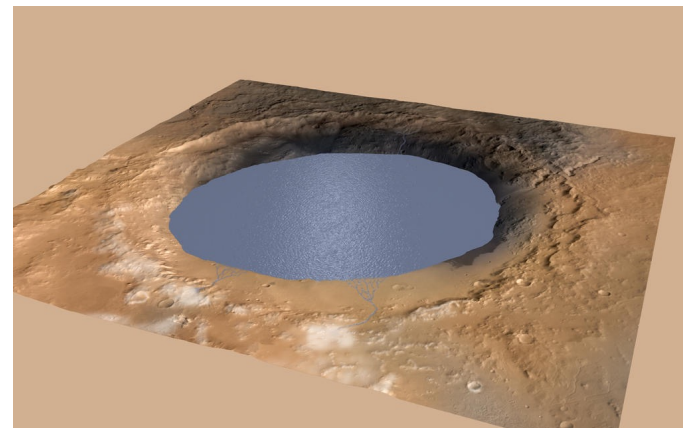
→ CB site was drilled in 2013! It takes time to perform quality analyses of unknown Mars samples, even with the most relevant instruments

CRATÈRE GALE: HABITABLE! MAIS HABITÉ??

Ancien Mars était *habitable*, il y a 3.8 Ga

Gale Crater était un lac d'eau douce

-> Curiosity recherche maintenant des molécules organiques complexes. SAM va continuer à nous surprendre!



Molécules primordiales/simples



Molécules prébiotiques



Molécules biologiques



Complexification chimique

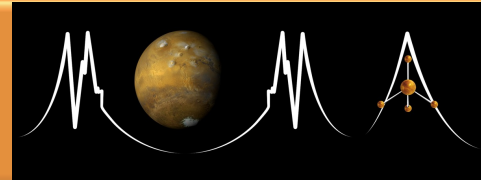


**ENANTIOMERIC DERIVATIZATION ON THE MARS
ORGANIC MOLECULE ANALYZER (MOMA)
EXPERIMENT ONBOARD EXOMARS 2028:
HOW TO UNRAVEL MARTIAN CHIRALITY**





ESA / ExoMars 2022



Launch: 2028 (?)

Duration: 218 sols

ExoMars Program Objective:

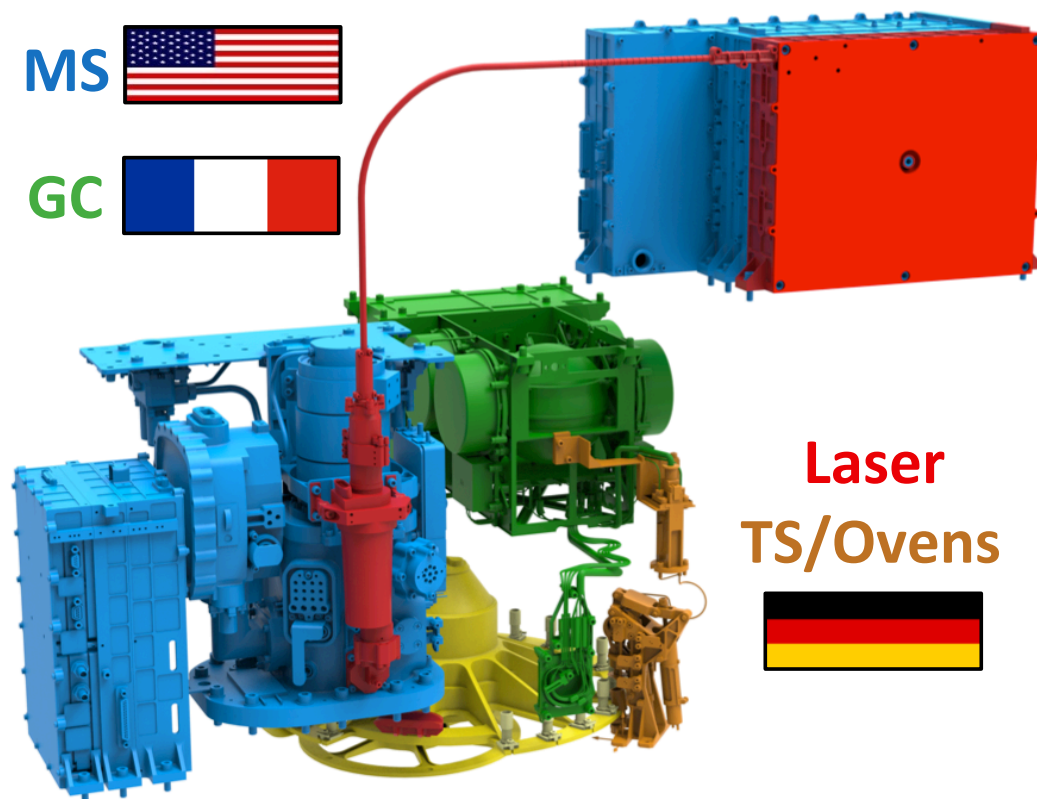
- Establish if life ever existed on Mars

ExoMars Rover Science Goals:

1. Search for signs of past and present life in the Mars (sub)surface
2. Investigate the water/geochemical environment versus depth

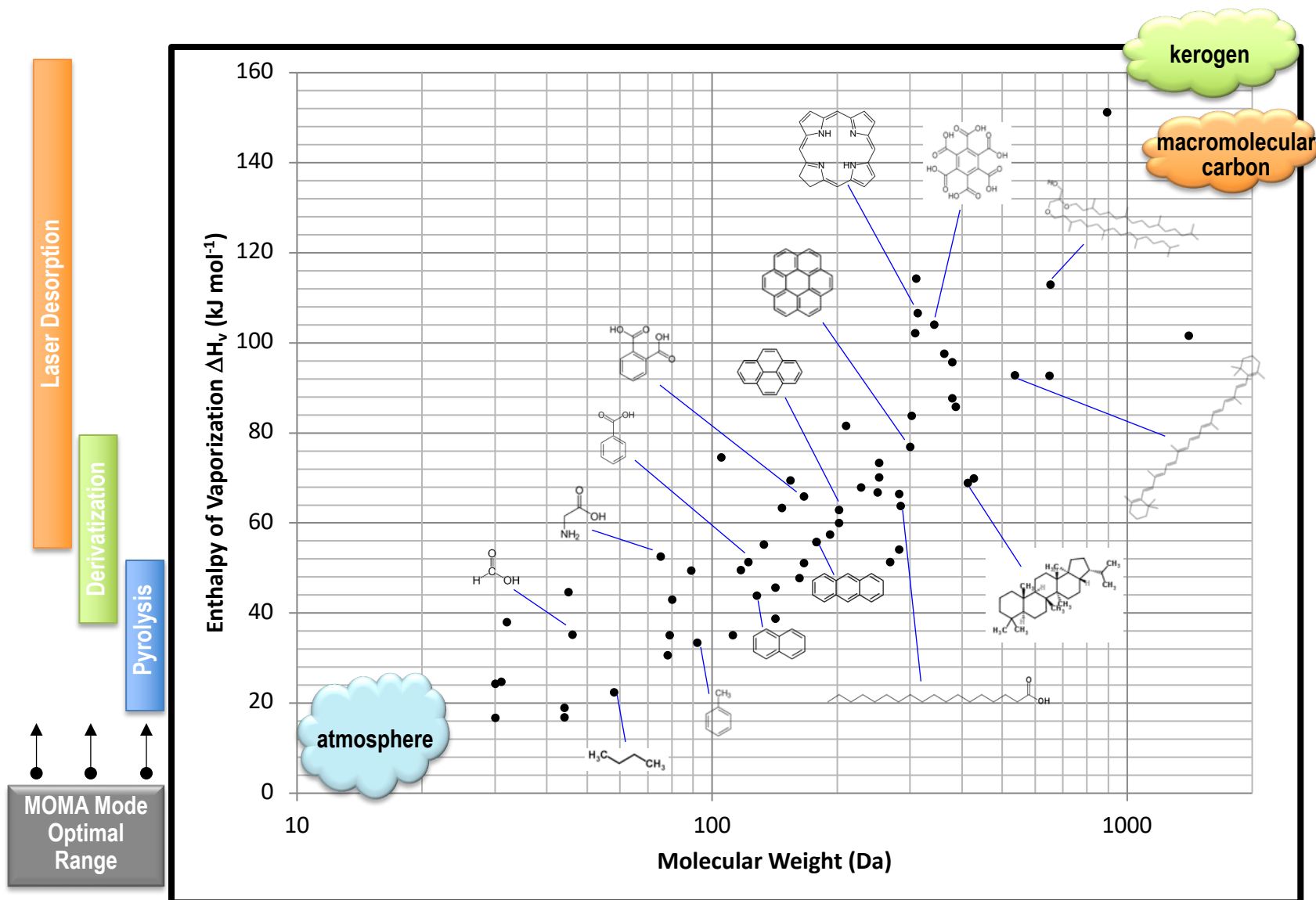
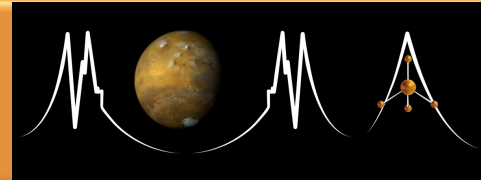
MS 

GC 

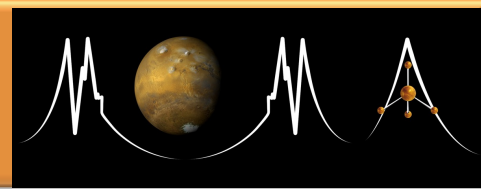


Laser
TS/Ovens





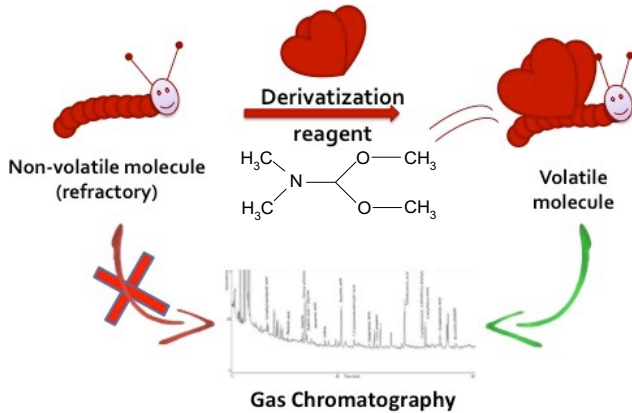
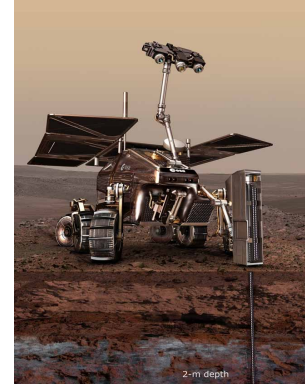
EN QUOI MOMA EST-IL "MIEUX" QUE SAM?



1 – Mars Organic Molecules Analyzer (MOMA) samples will be **drilled down to 2 meters deep**

Organics are prone to degradation under cosmic radiations.

Preserved samples are buried < 2-3 m

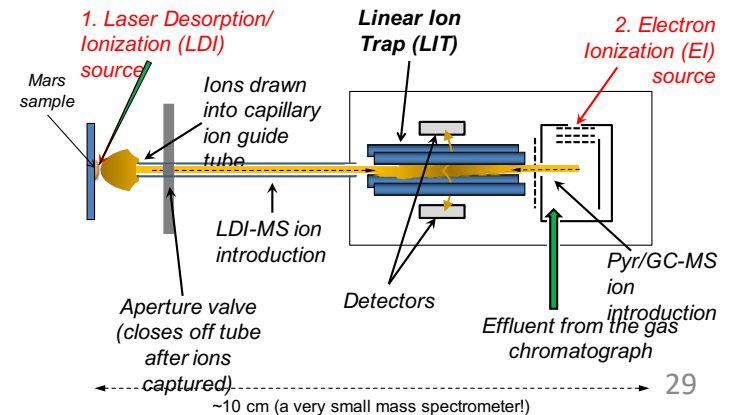


2 - DMF-DMA Derivatization / Gas Chromatography-Mass Spectrometry

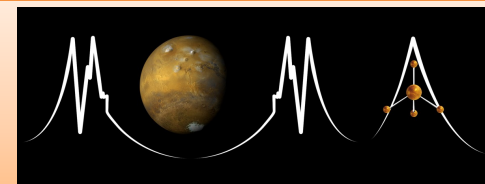
Targets: Carboxylic acids, Amino acids, Nucleobases, Amines, Alcohols, Sugars, specific molecular distributions

3 – Laser desorption/ionization - Mass Spectrometry

Targets: macromolecular carbon and biosignatures, repetitive mass patterns, specific molecular distributions



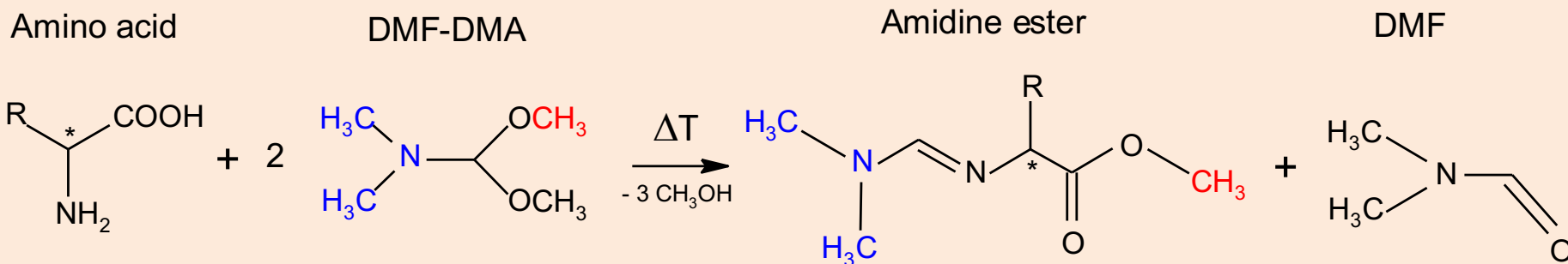
The origin of organics: biotic or abiotic?



DMF-DMA Derivatization

N,N-dimethyl-formamide dimethylacetal

Single step reaction to transform less volatile organics (with H labile) into methylated derivatives that can be detected by GC-MS.

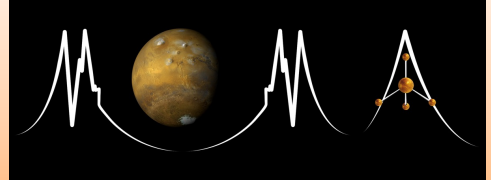


Protects the asymmetrical center(s) of the derivatized molecules

-> constraining the nature and origin of the organic compounds detected on Mars to look for possible past or present biosignatures



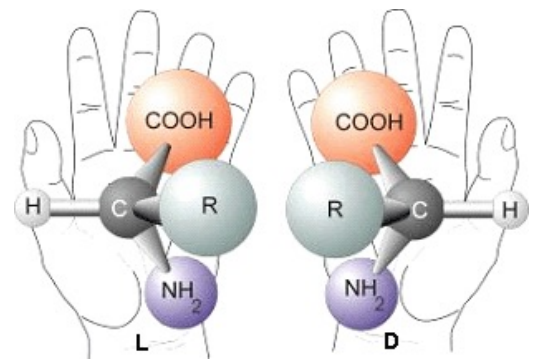
Homochirality as an indicator of life?



Lord Kelvin 1904 : « I call any geometrical figure, or group of points, chiral, and say it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself »

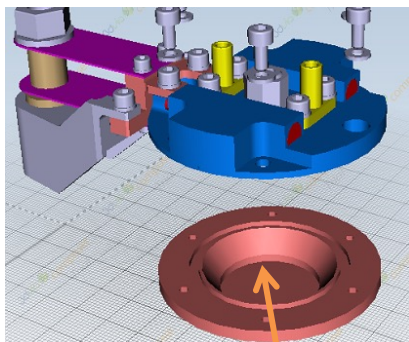
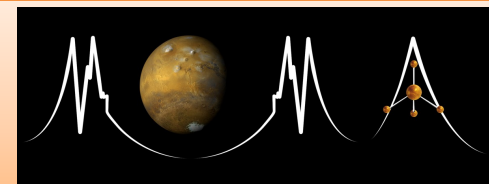
Chirality → 2 enantiomers

	Abiotic	Biotic (life)
Amino acids	L / D	L
Glucids	L / D	D



Homochirality, feature of life.

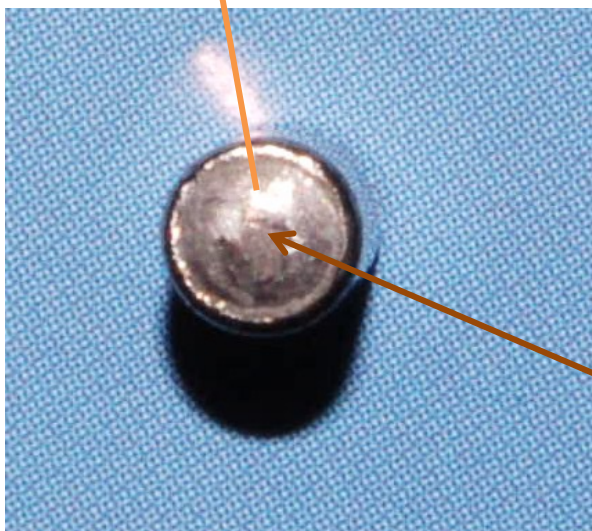
MOMA derivatization capsules



The derivatization reagent is released at a chosen temperature

$\phi = 3.6 \text{ mm}$
High = 5 mm
Material: Stainless steel
Eutectic : InSn, PbSn, AgSn
Capacity: 15 μL

Before derivatization



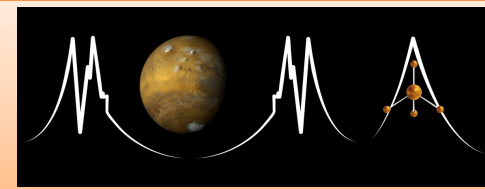
Eutectic



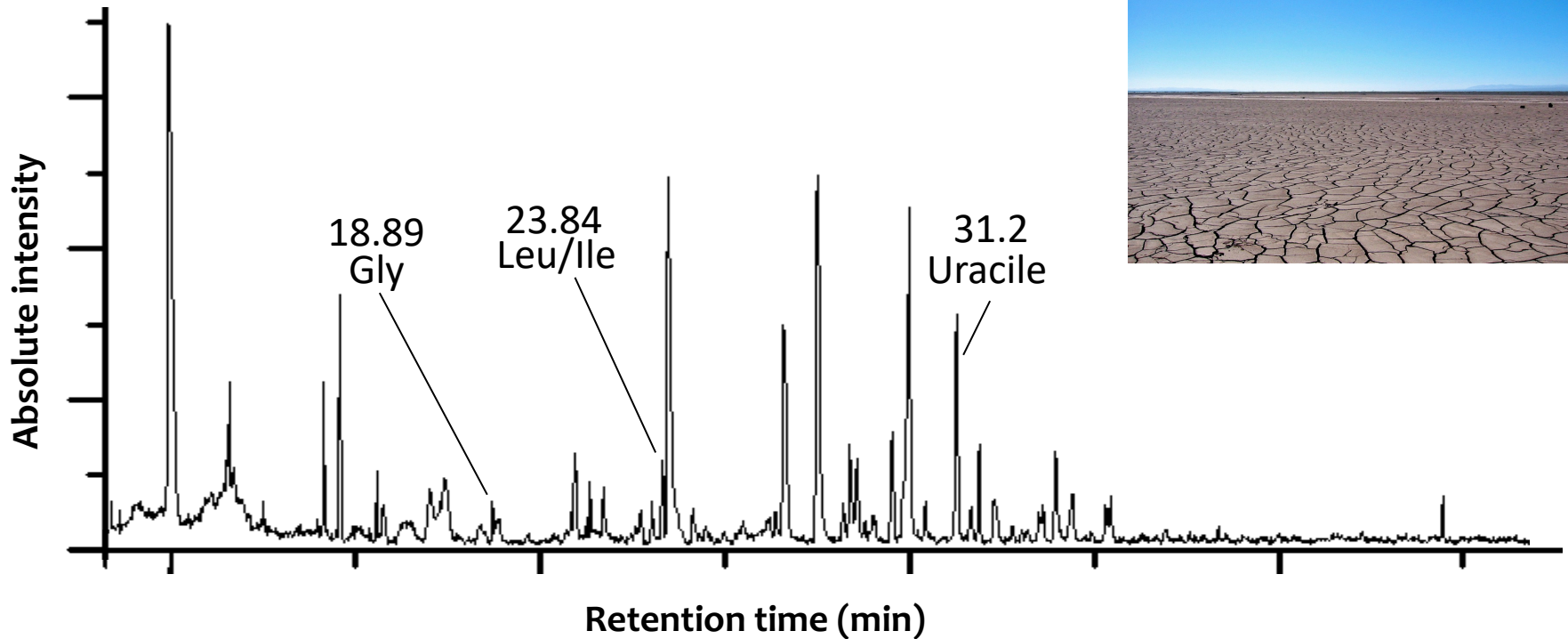
After derivatization



Extraction-derivatization One-pot/one-step



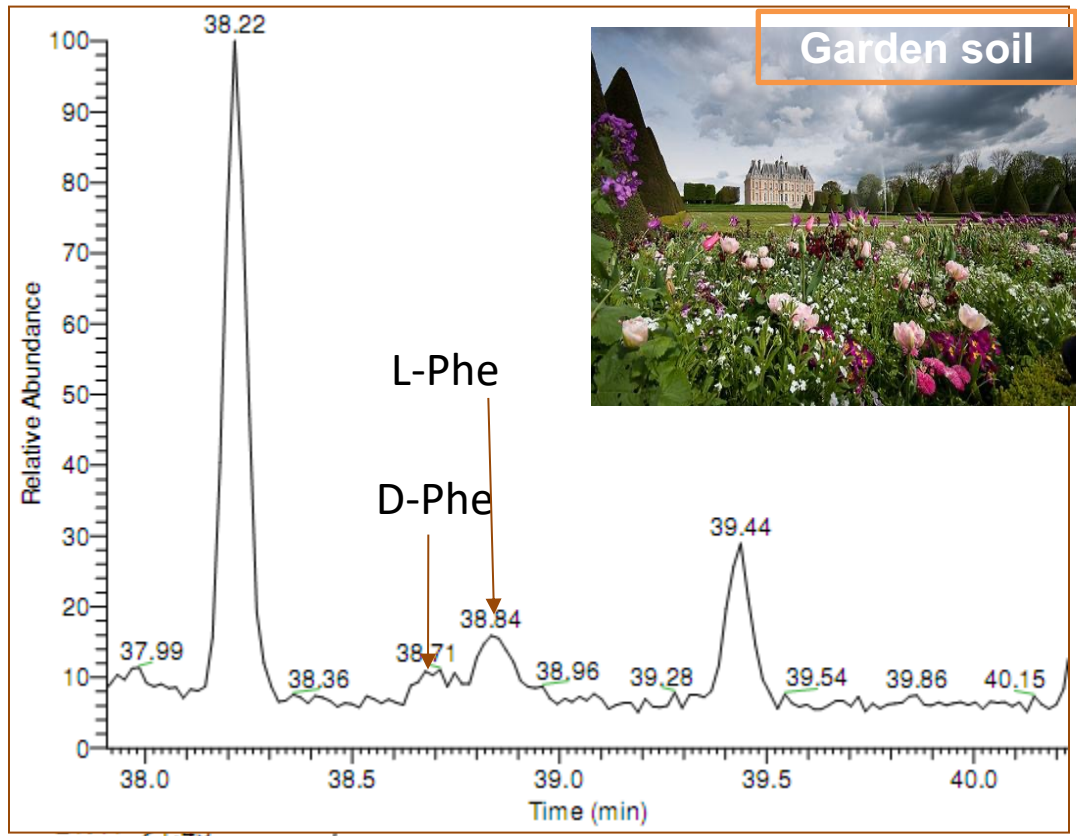
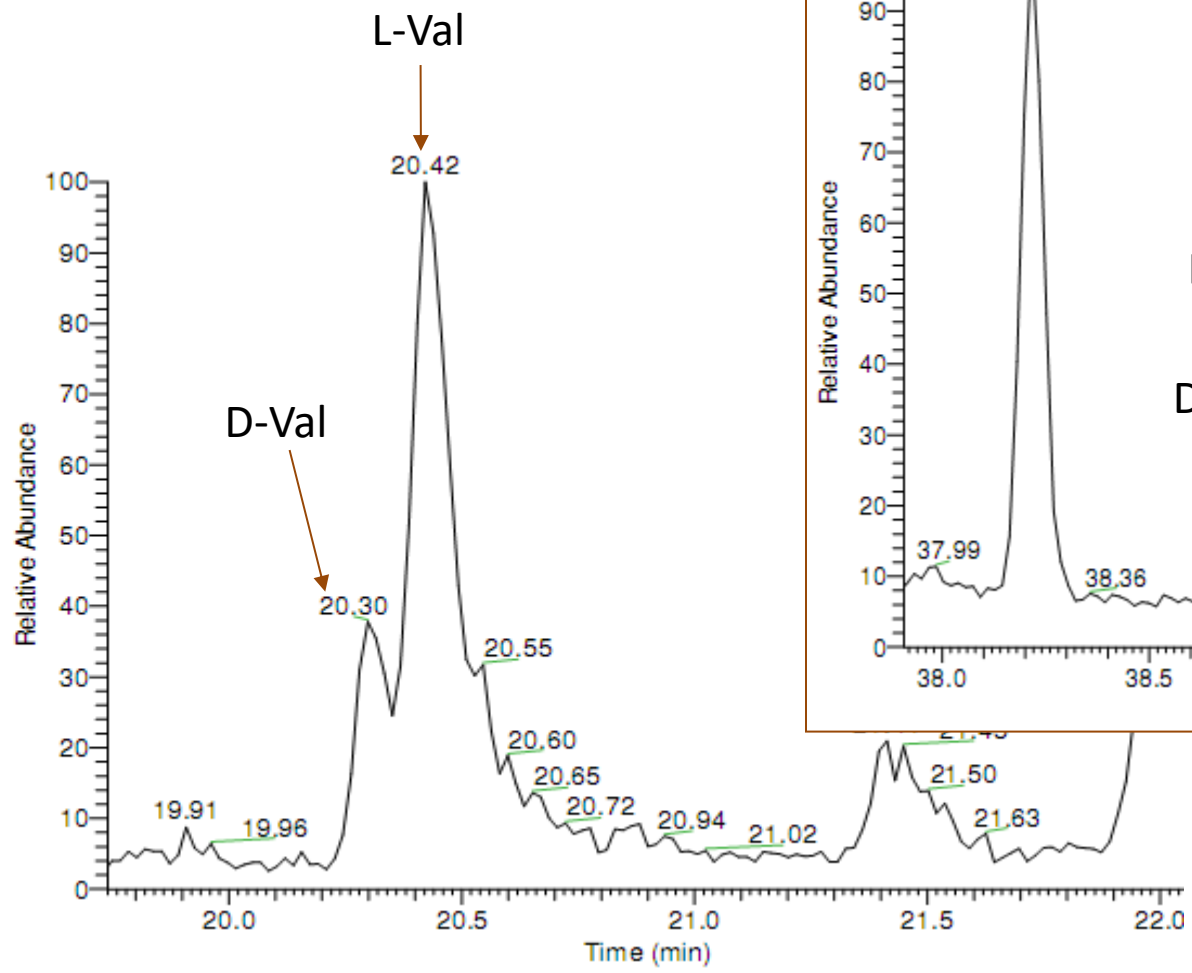
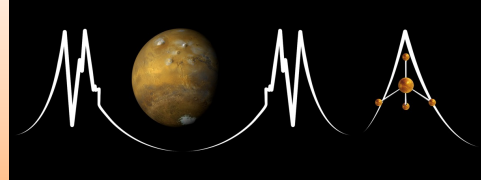
Atacama desert (Chile)



Preliminary results → Amino acids and nucleic base detected



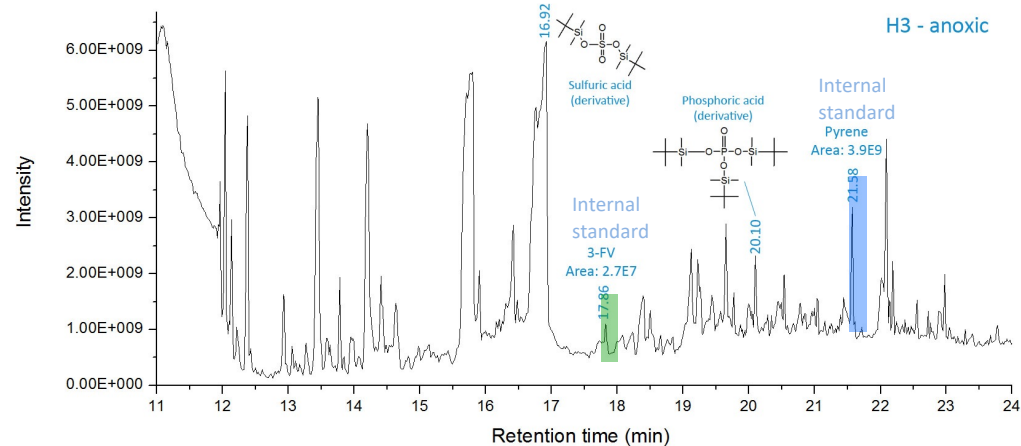
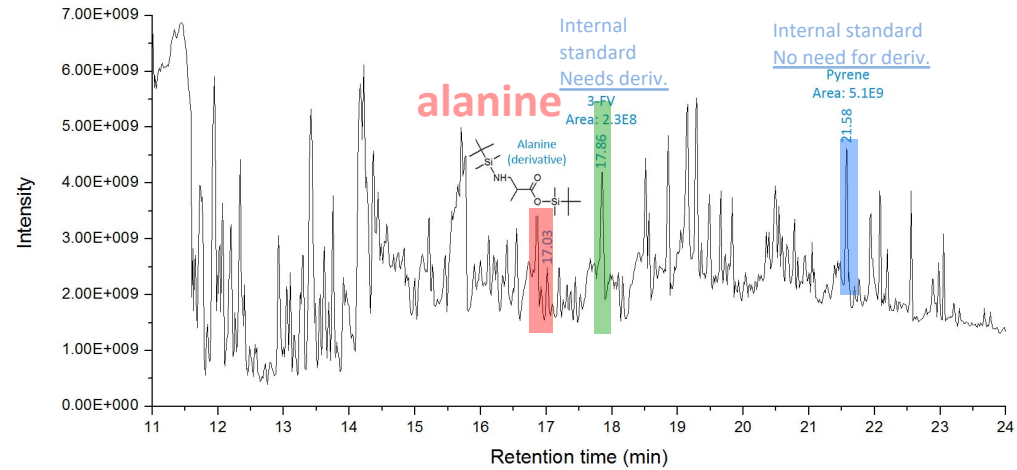
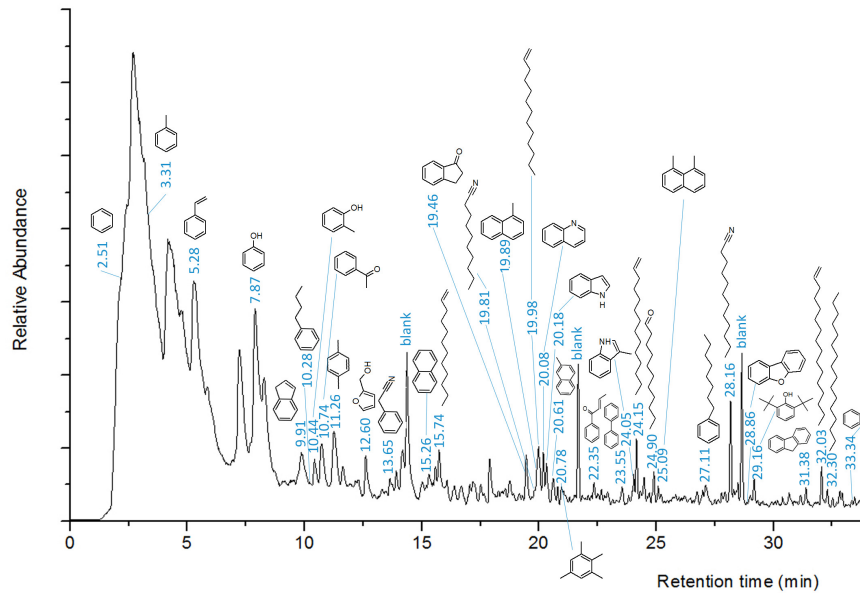
Enantiomeric separation



→ Chiral separation Ala – Val – Phe
→ Without total racemization

Pyrolysis vs. derivatization for organics detection

Mars Analog Experiments: Lake Hoare Sediment, Antarctica



Derivatization-GC/MS:

- detection of complex, polar and refractory molecules
- protection of molecules – Reaction at mild temperatures (~300°C)

Pyrolysis-GC/MS:

- detection of simple, non-polar and volatile aromatics and aliphatics
- break down of high molecular weight organics (high temperature pyrolysis)

LA TÊTE DANS LES ÉTOILES

Mars



2021
Perseverance



ExoMars 2028

Jupiter



EUROPA LANDER MISSION
JPL D-57857
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EUROPA LANDER MISSION PAGE 4



Juice 2023
24 avril

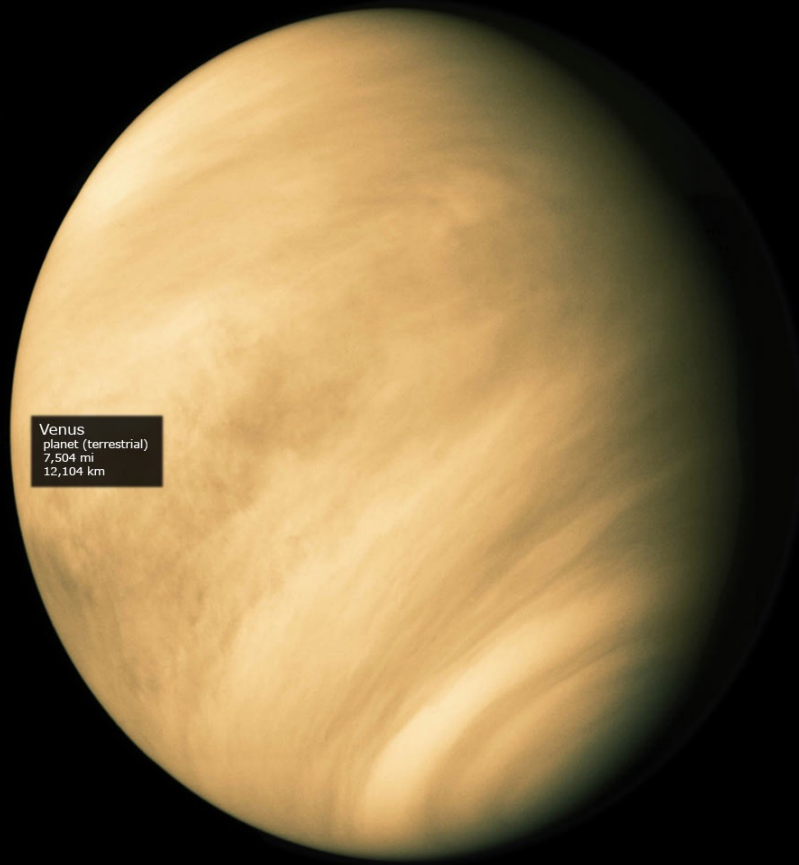
Saturne



Dragonfly 2034



Des dizaines de **mondes** dans le système solaire (~60 corps > 300 km)



Venus
planet (terrestrial)
7,504 mi
12,104 km



Mars
planet (terrestrial)
4,204 mi
6,780 km