Chemical automata at the origin of life

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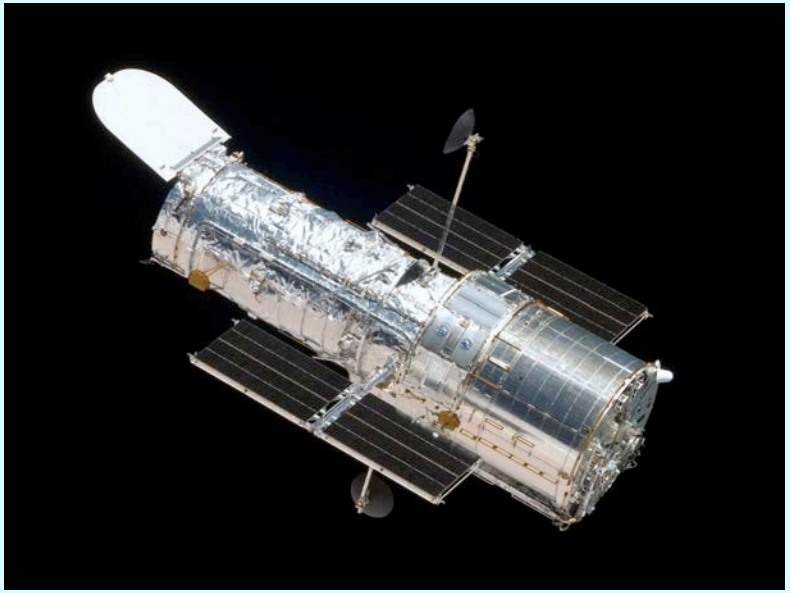
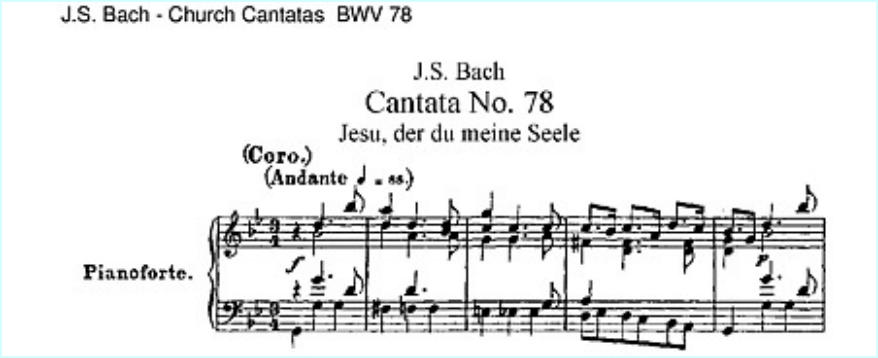
Supernova G299 in the Milky Way

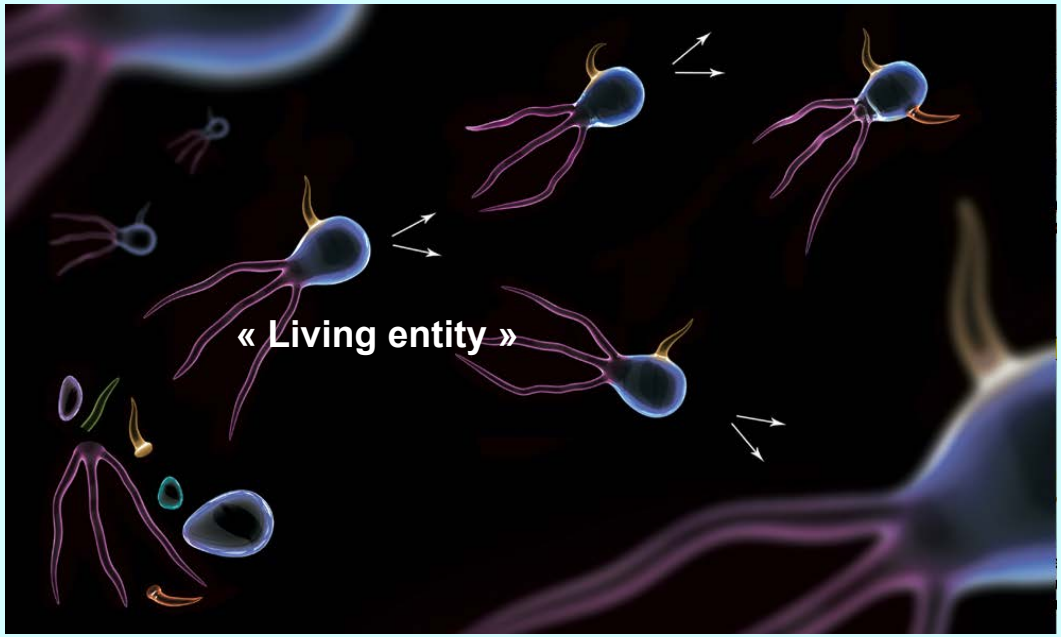
In « Terre des Hommes », Antoine de Saint-Exupéry wrote in February, 1939:

«of a lava in fusion, a paste of stars, a living cell germinated miraculously we came, and, little by little, we rose to the point of writing cantatas and weighting milky ways»





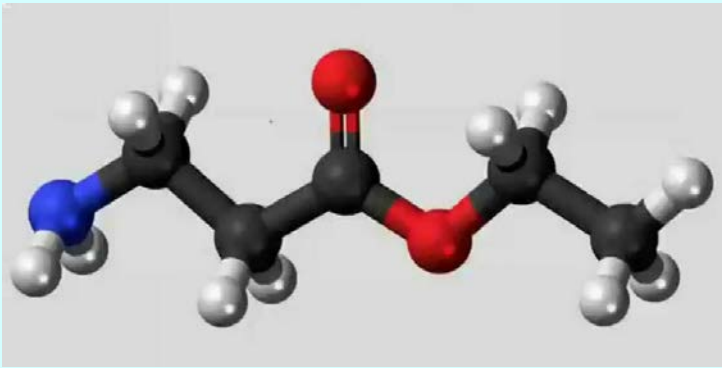
On Earth, life emerged in water, about 4 Ga years ago with chemical automata capable of making more of theselves by themselves and of evolving.

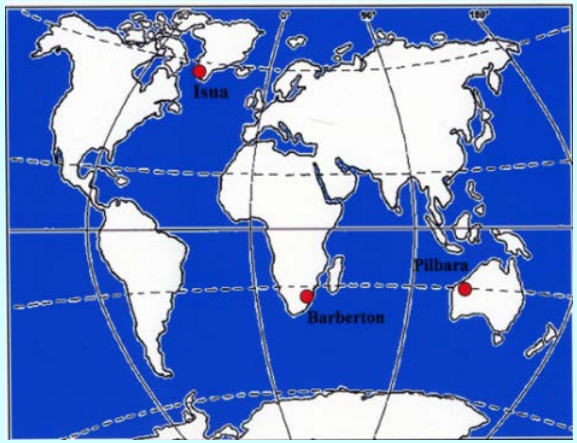


The pieces were organic molecules, i.e. carbon atom scaffoldings garnished with hydrogen, oxygen, nitrogen, atoms.

Chemist's concerns:

- **Origin of water?**
- **Origin of organics?**
- **Recreate an automata?**
- **Fossils?**



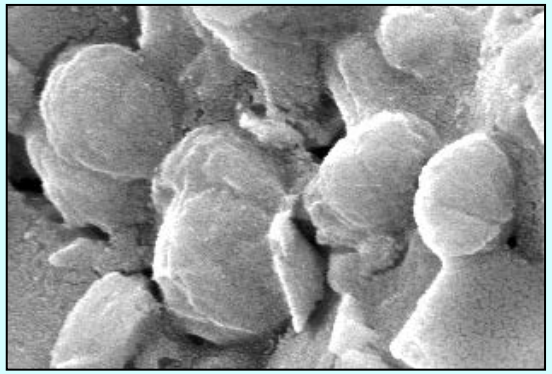


Early traces of life

Frances Westall, Orléans

3,8 Ga. Isua?

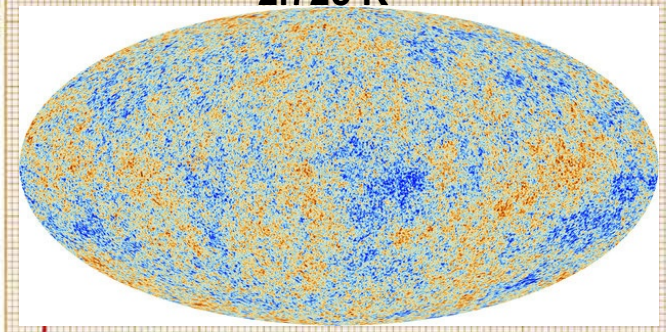
3,45 Ga. stromatolites

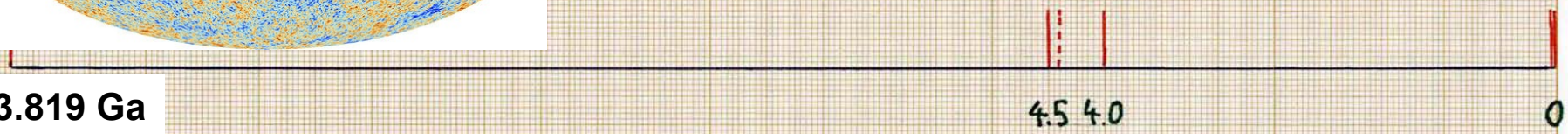


3,334 Ga. Microfossiles

Water at the origins

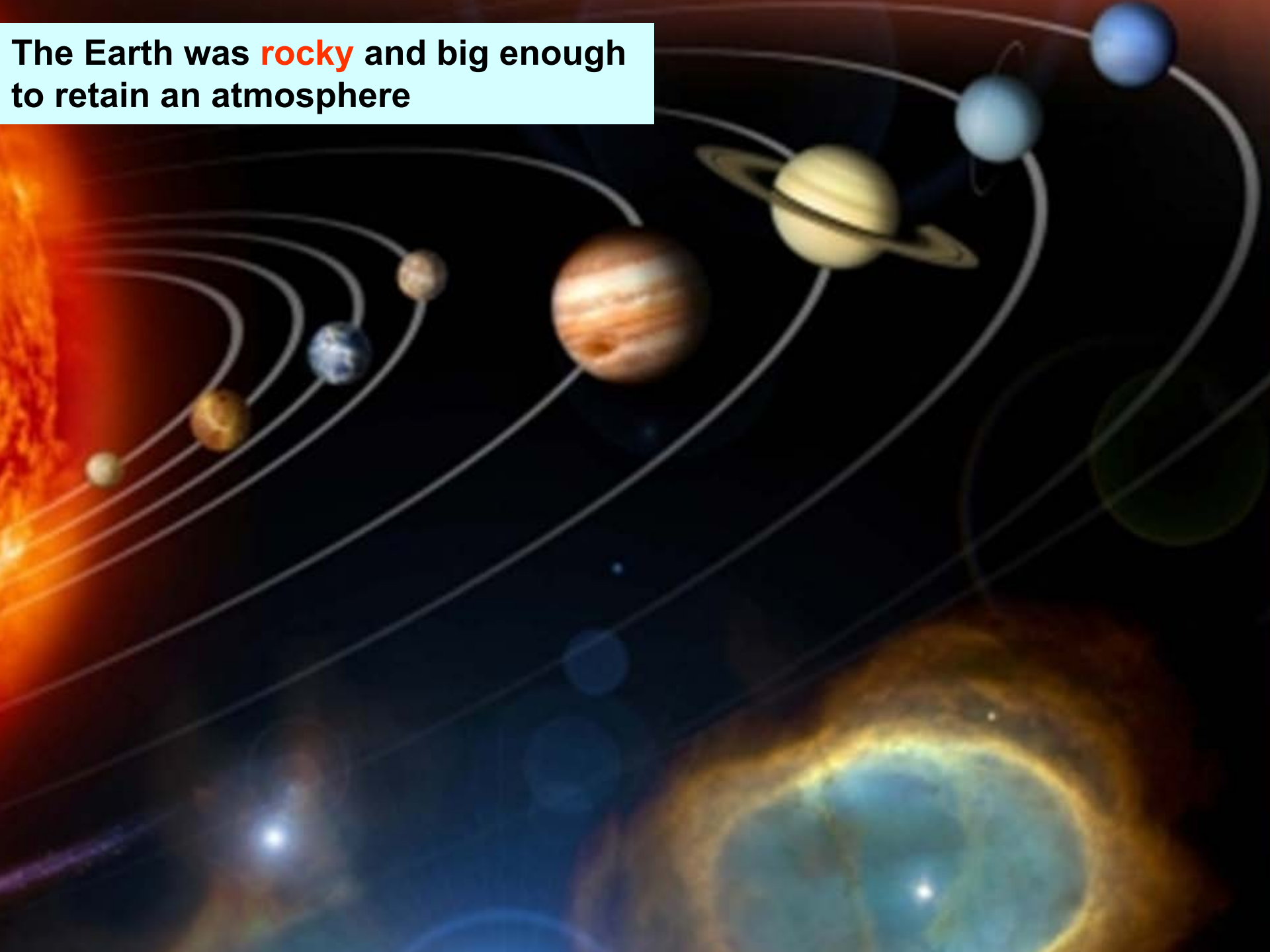
Cosmic Microwave Background
2.725 K





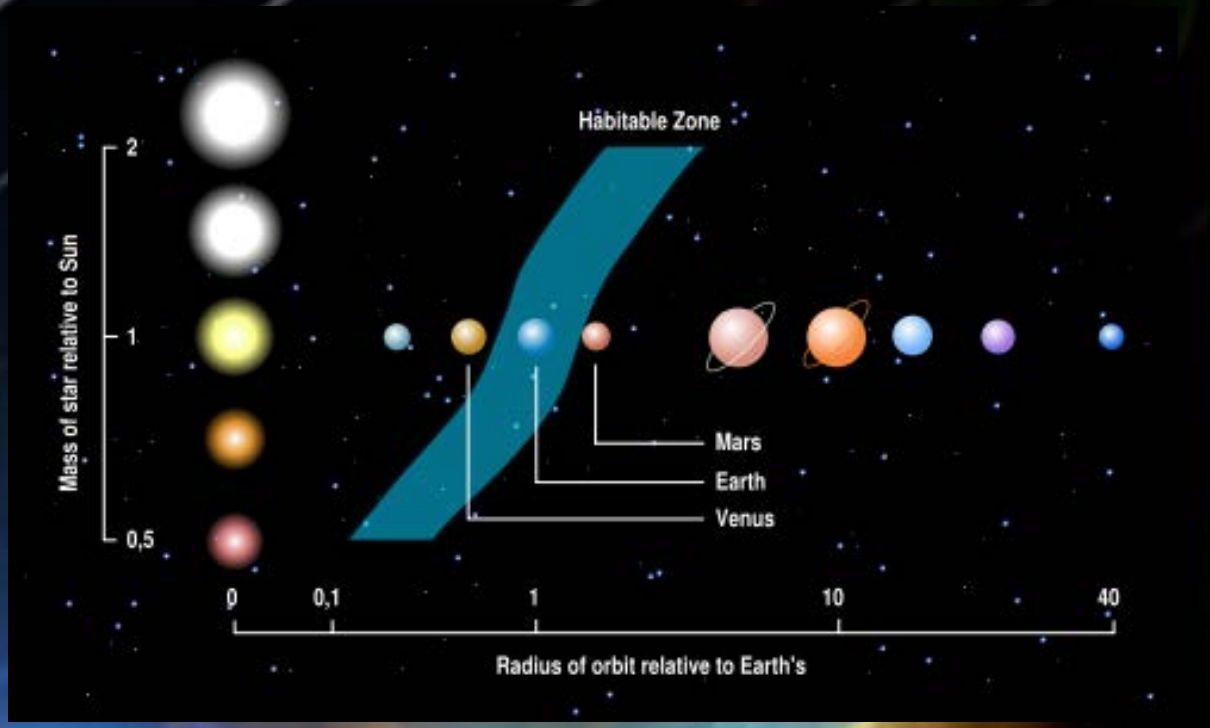
3.819 Ga

4.4 Ga years old zircon (zirconium silicates with datable traces of uranium and thorium) have been processed by liquid water, as testified by oxygen isotope ratios.

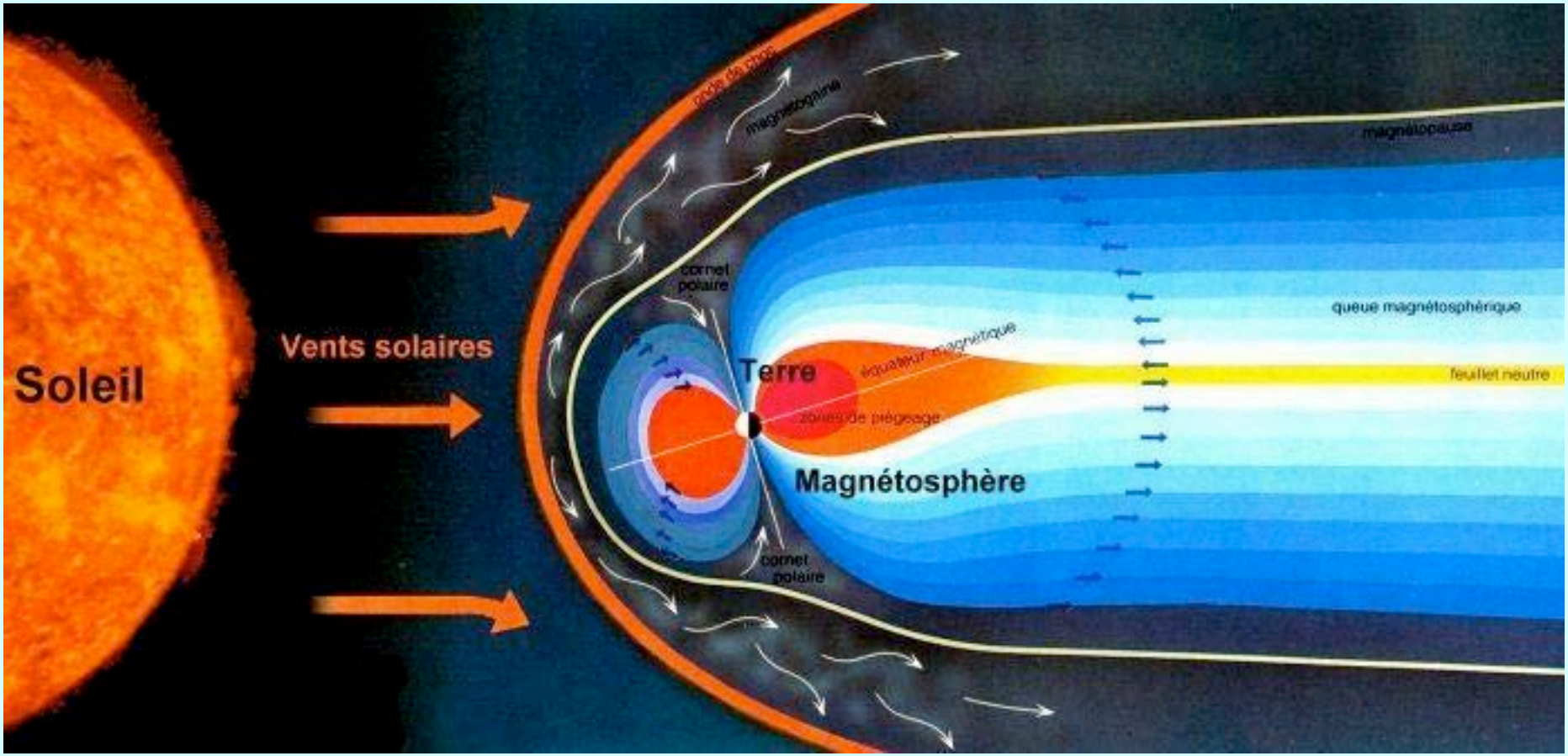

The Earth was rocky and big enough
to retain an atmosphere

- not too close to the Sun (divergent green house),
- not too far (glaciation)

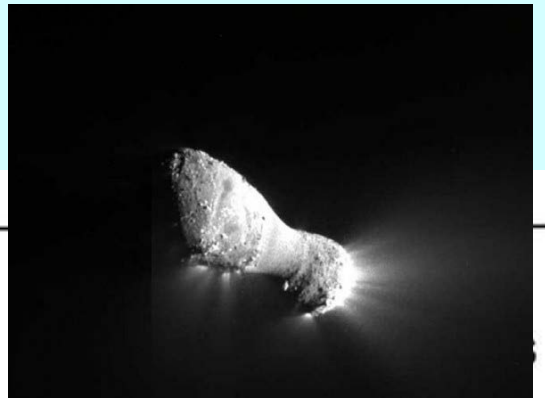
In the so-called « habitable zone »



The Earth has a permanent magnetic field which generate a magnetosphere protecting from the air-corrosive solar wind.

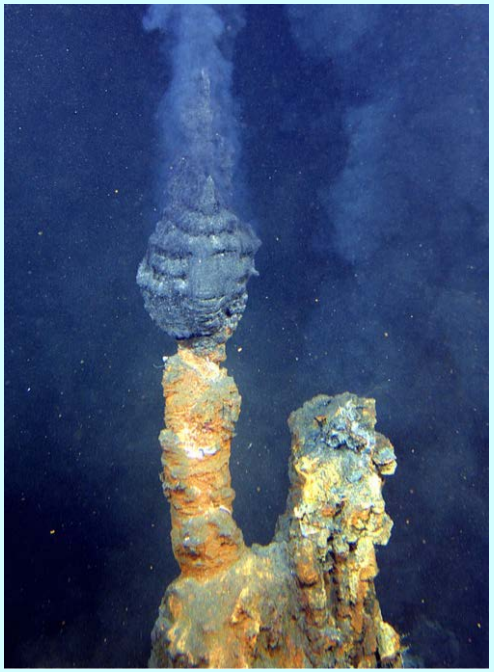


Late veneer of cometary water?



Three possible sources for prebiotic organic carbon:

1) Atmosphere

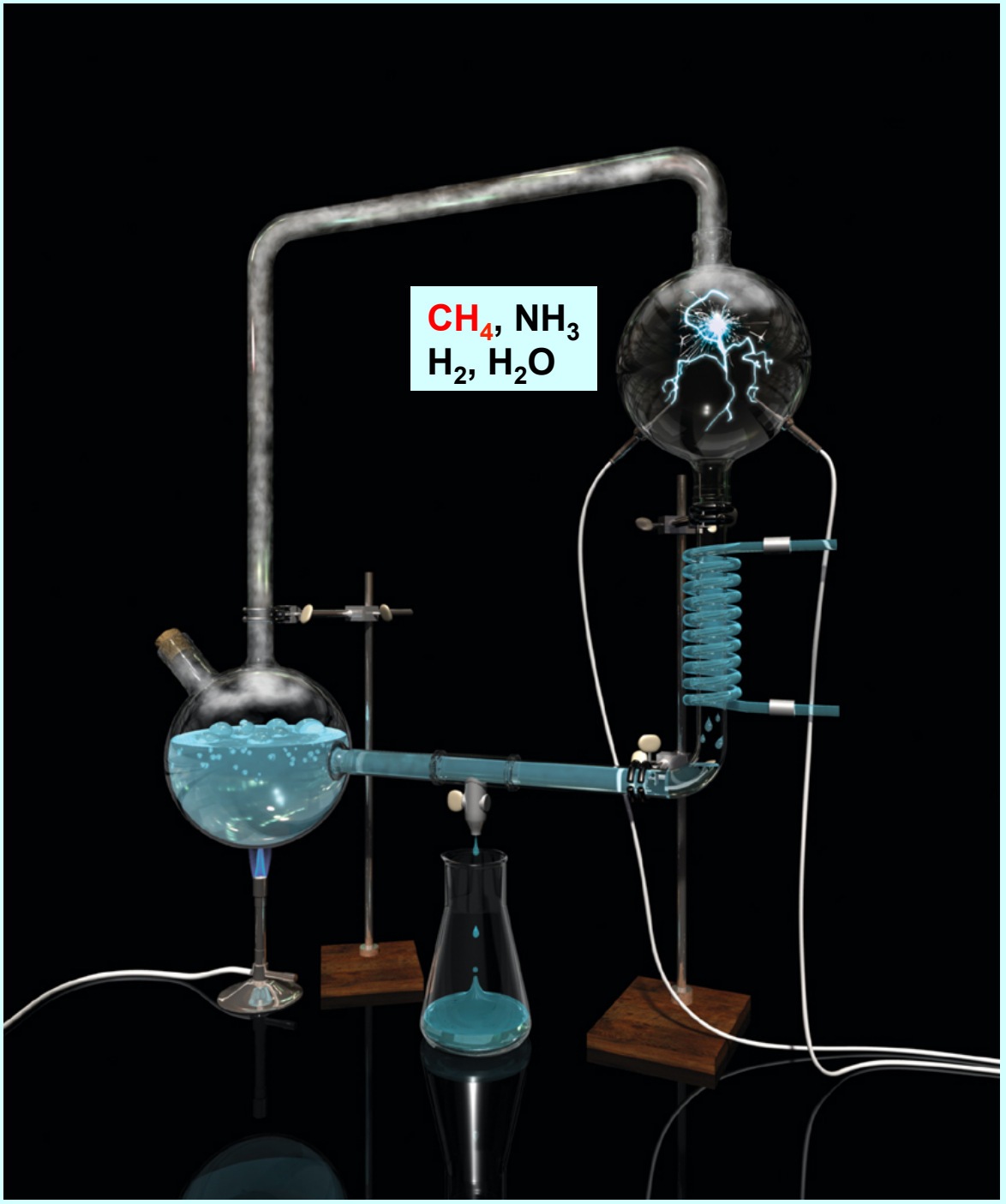


2) Hydrothermal systems

3) Space

Miller experiment for the prebiotic synthesis of amino acids

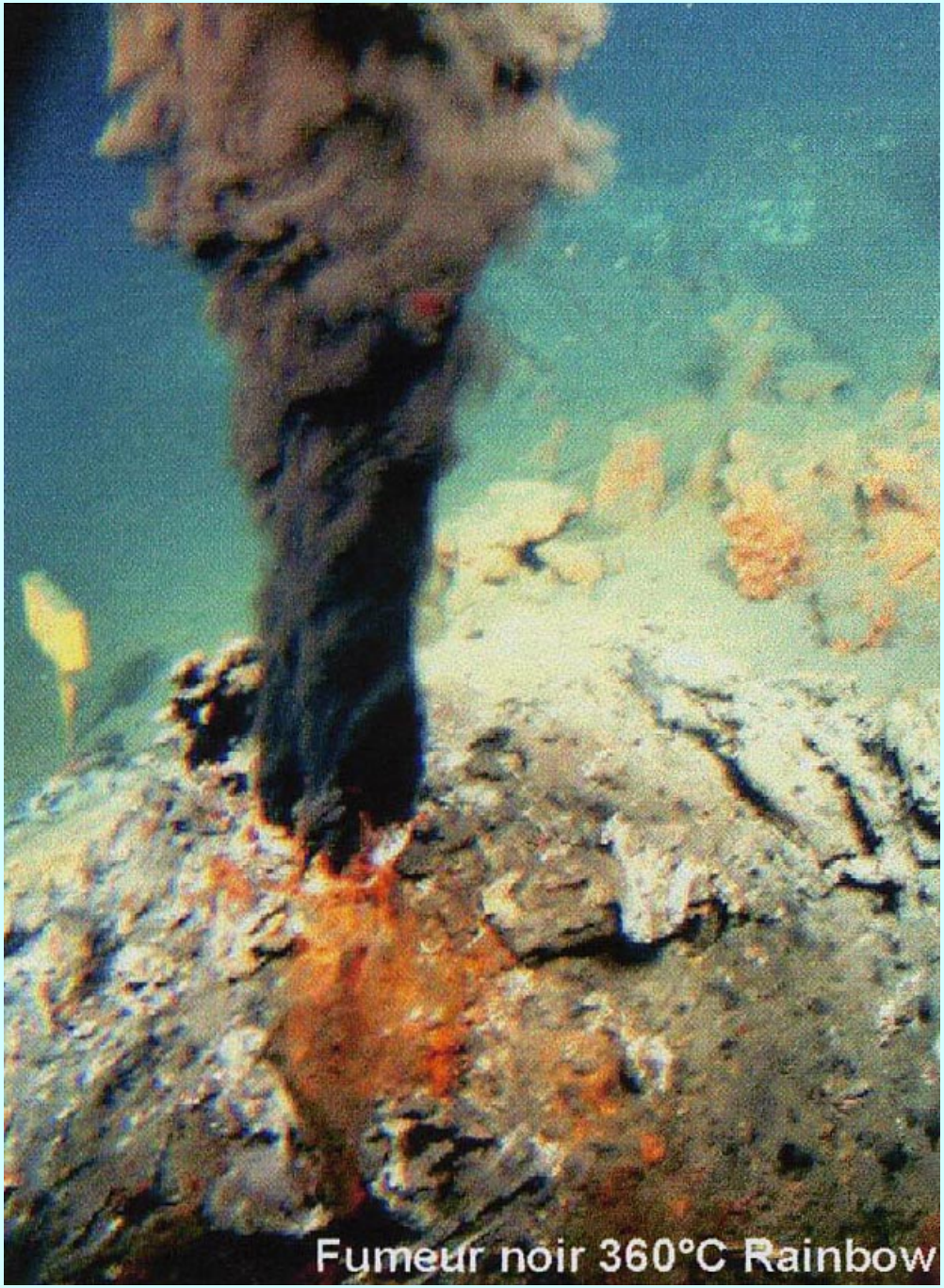
- **But there was very few methane in the primitive atmosphere**



Rainbow submarine hydrothermal system

- **No prebiotic molecules detected so far**

Gas	%
Hydrogen	45
Methane	6
Carbon dioxide	43
Nitrogen	4
Hydrogen sulfide	2



Murchison meteorite

Biological compounds in Murchison

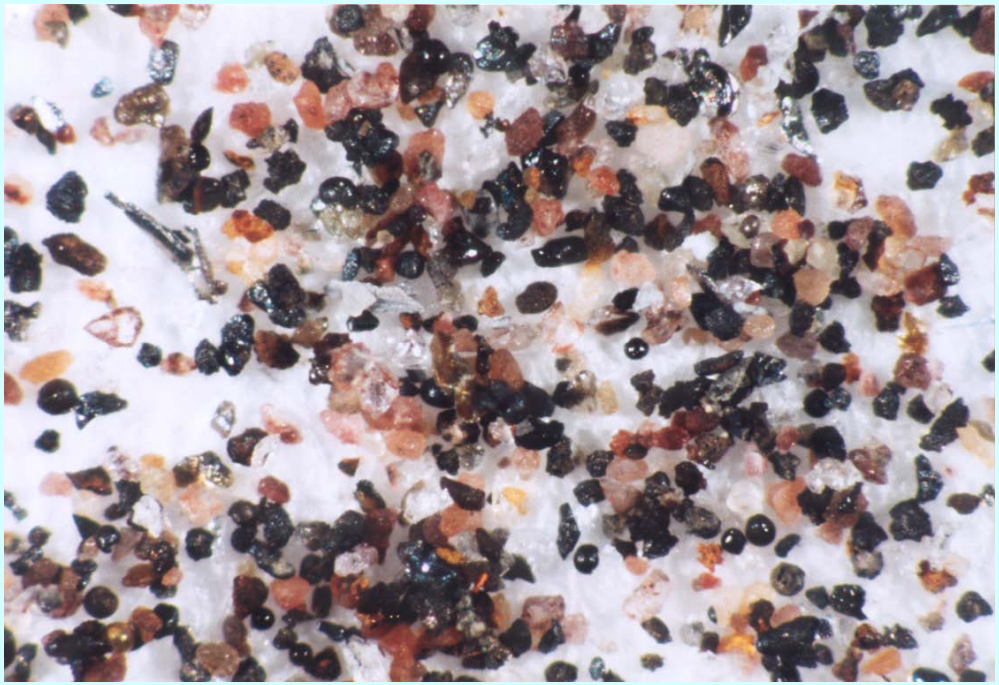
Glycine	C_2-C_{12} carboxylic acid	Adenine
Alanine	Lactic acid	Guanine
Valine	β-hydroxy butyric acid	Xantine
Leucine	Malic acid	Hypoxantine
Isoleucine	Succinic acid	Uracil
Proline	Fumaric/maleic acid	
Aspartic acid	Acetone	
Glutamic acid	Urea	
	Ethanol	

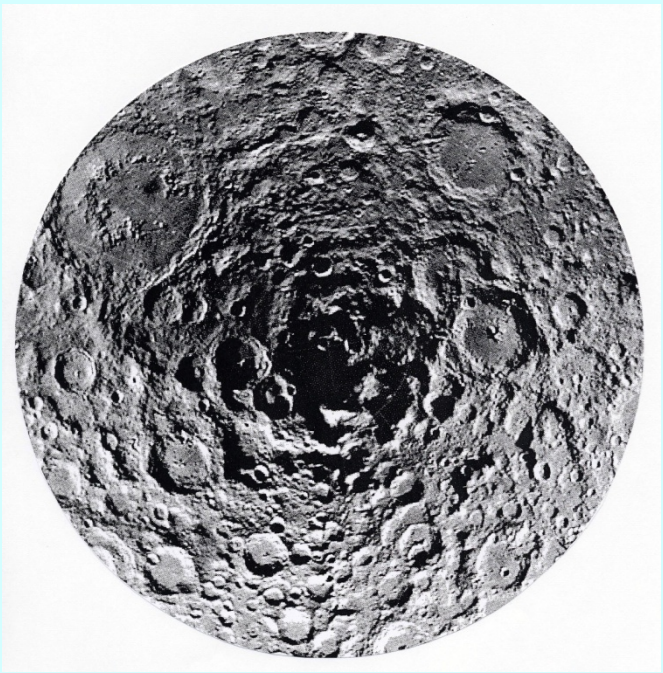
Rather modest delivery per year: today, « only » 100 tonnes

Micrometeorites: from collection and heavy bombardment

⬇

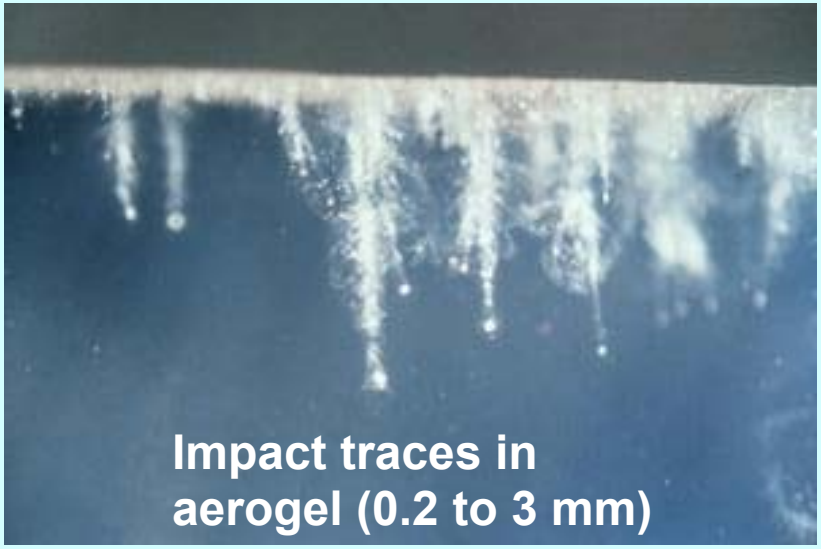
Organic matter delivered during the heavy bombardment represented 25 000 times that of the present biomass, i.e. a 30 m thick layer of « oil slick » cumulated all over the globe.





The Stardust mission

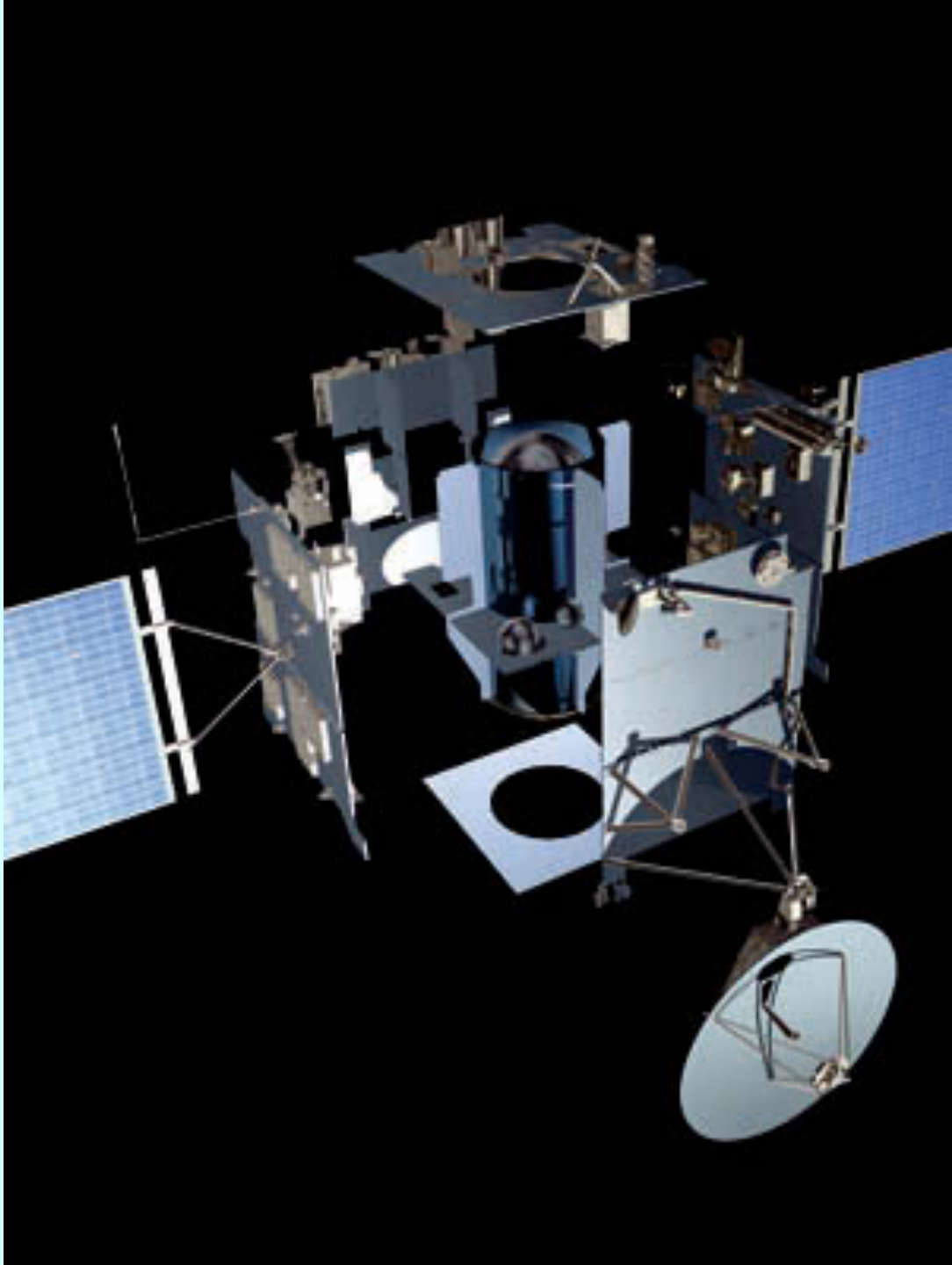
Launched in1999, the probe collected cometary dust of Wild 2 on January 2004. The capsule landed on January 2006 in Utah desert.



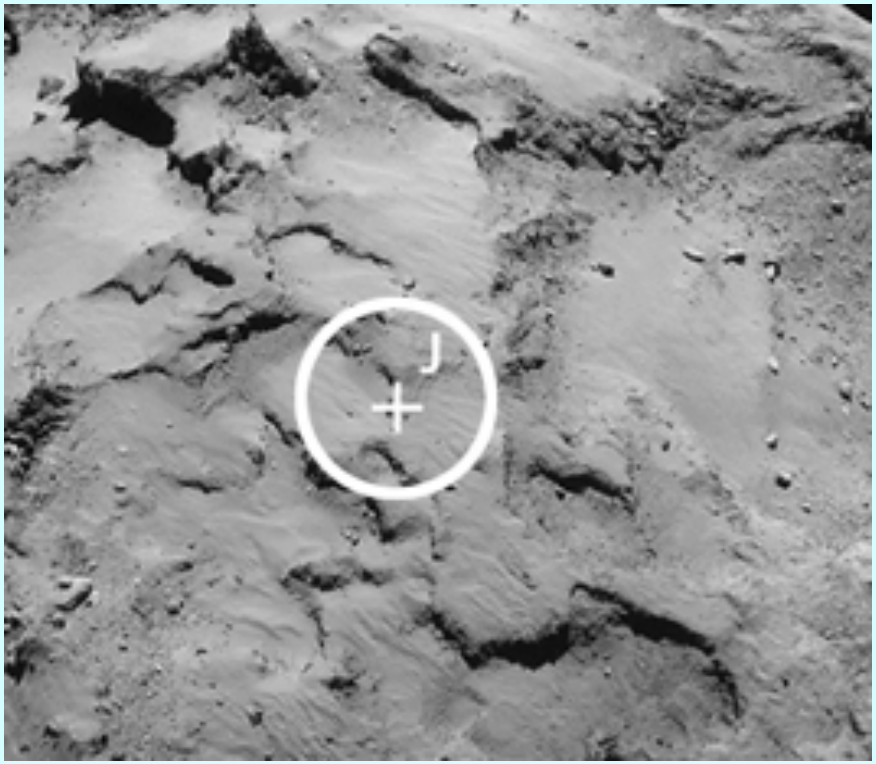
The grains contain organic matter (identified functions: alcohol, cetone, aldehyde, carboxylic acid, amide, nitrile, glycine, etc.)

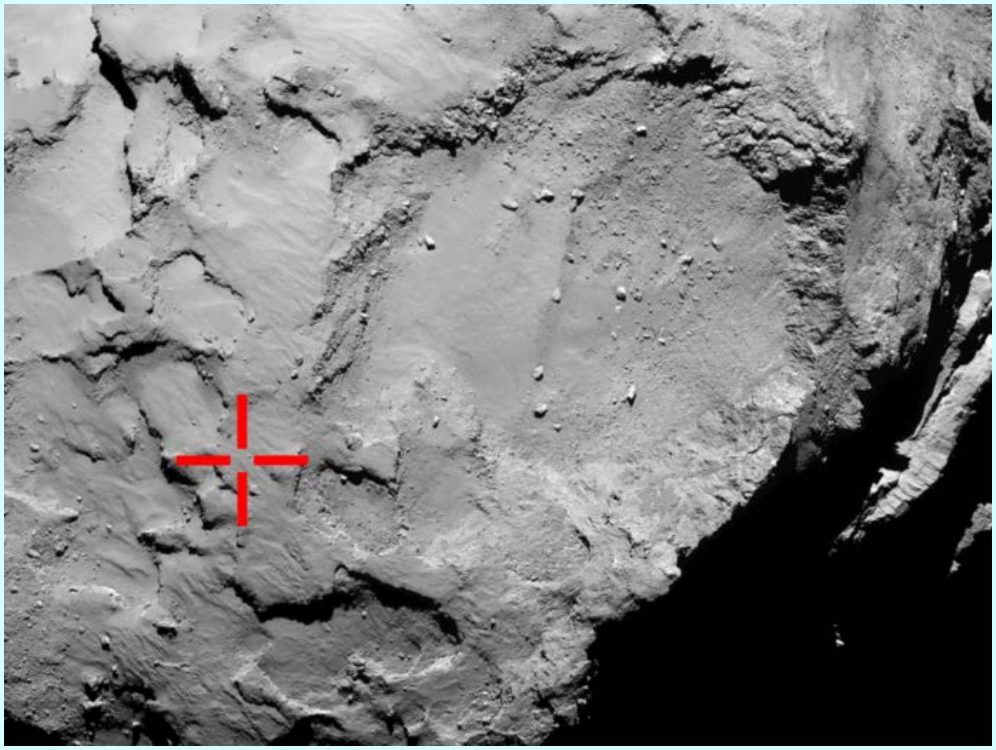
The micrometeorites are cometary in origin.

The Rosetta probe to comet Churyumov-Gerasimenko.
Launched : 2 march 2004
Arrived August 2014
(4 gravitational assistance, 3 Earth, 1 Mars)




Philae landed here





Philae bumped twice ...

... before immobilizing in a ridiculous position

Outcome

- 16 molecules were detected by Philae in the splinters during the first bump

- glycine was detected by Rosetta

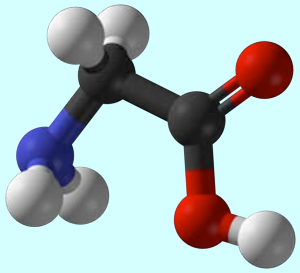
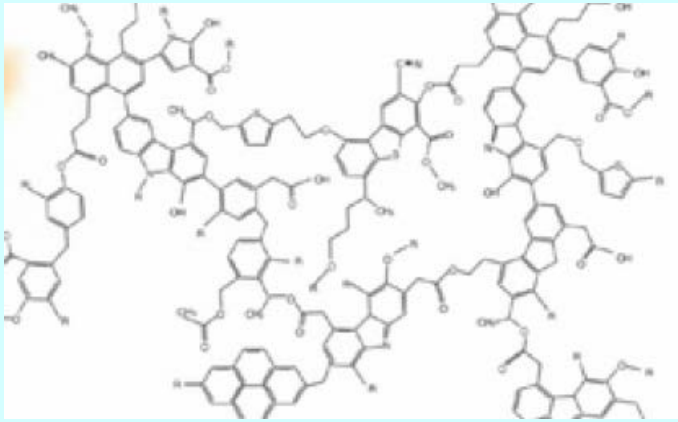


Table 1. The 16 molecules used to fit the COSAC mass spectrum.

Name	Formula	Molar mass (u)	MS fraction	Relative to water
Water	H_2O	18	80.92	100
Methane	CH_4	16	0.70	0.5
Methanenitrile (hydrogen cyanide)	HCN	27	1.06	0.9
Carbon monoxide	CO	28	1.09	1.2
Methylamine	CH_3NH_2	31	1.19	0.6
Ethanenitrile (acetonitrile)	CH_3CN	41	0.55	0.3
Isocyanic acid	HNCO	43	0.47	0.3
• Ethanal (acetaldehyde)	CH_3CHO	44	1.01	0.5
Methanamide (formamide)	$HCONH_2$	45	3.73	1.8
Ethylamine	$C_2H_5NH_2$	45	0.72	0.3
• Isocyanomethane (methyl isocyanate)	CH_3NCO	57	3.13	1.3
Propanone (acetone)	CH_3COCH_3	58	1.02	0.3
• Propanal (propionaldehyde)	C_2H_5CHO	58	0.44	0.1
• Ethanamide (acetamide)	CH_3CONH_2	59	2.20	0.7
• 2-Hydroxyethanal (glycolaldehyde)	CH_2OHCHO	60	0.98	0.4
1,2-Ethanediol (ethylene glycol)	$CH_2(OH)CH_2(OH)$	62	0.79	0.2



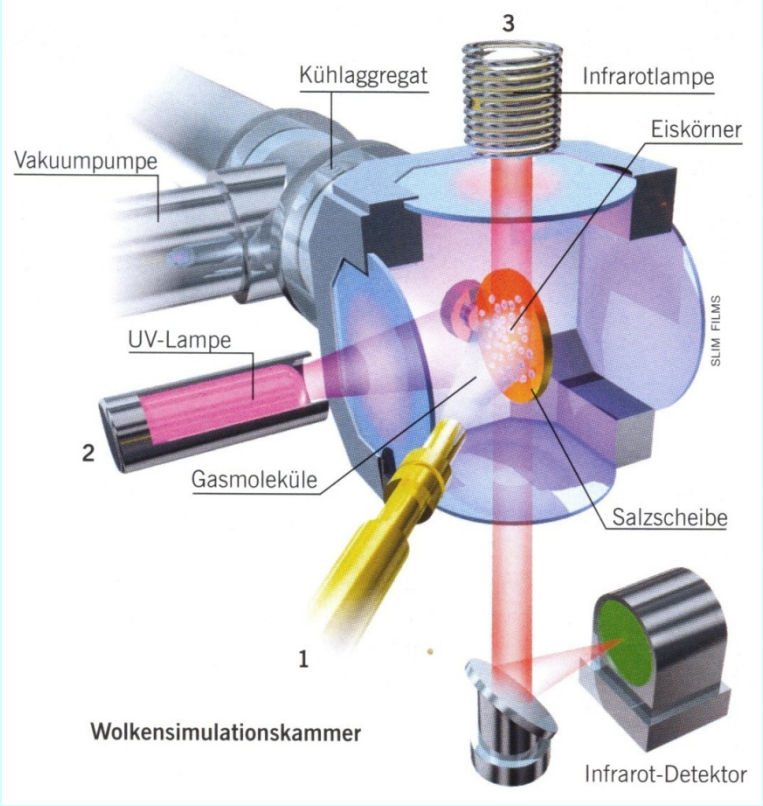
- Very complex organic matter was detected in the dust ejected by the nucleus

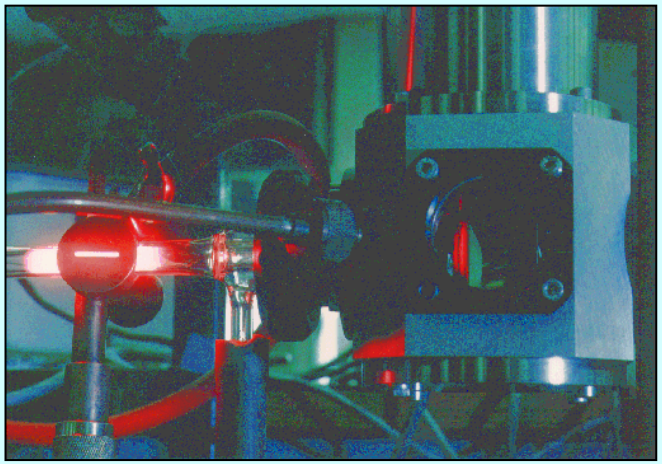
- Cometary water does not fit with terrestrial water (D/H).

- Comets could have delivered 22 % of our atmospheric xenon

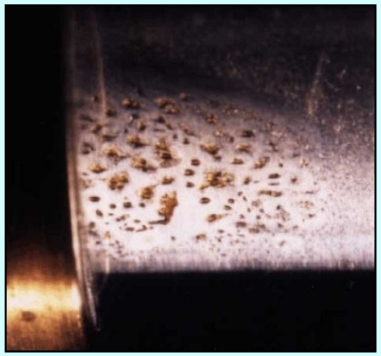
Mimicking interstellar chemistry produced amino acids in the lab

Ices of water, carbon monoxide and dioxide, methanol and ammonia (2,1,1,1,1) wer irradiated at 12 K in Leide.
16 amino acids were identified in Orléans.

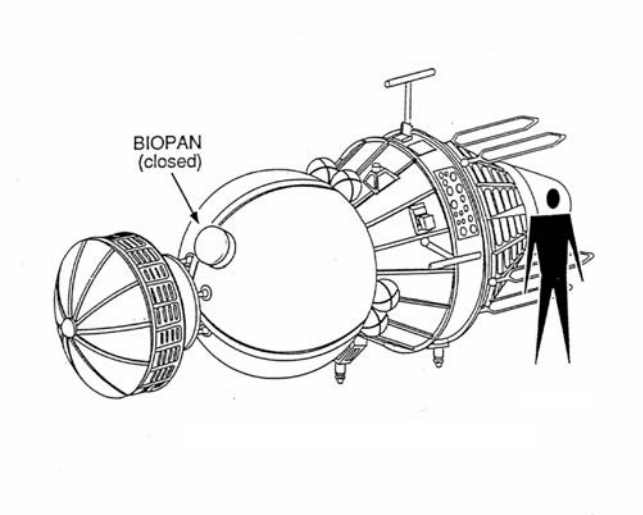


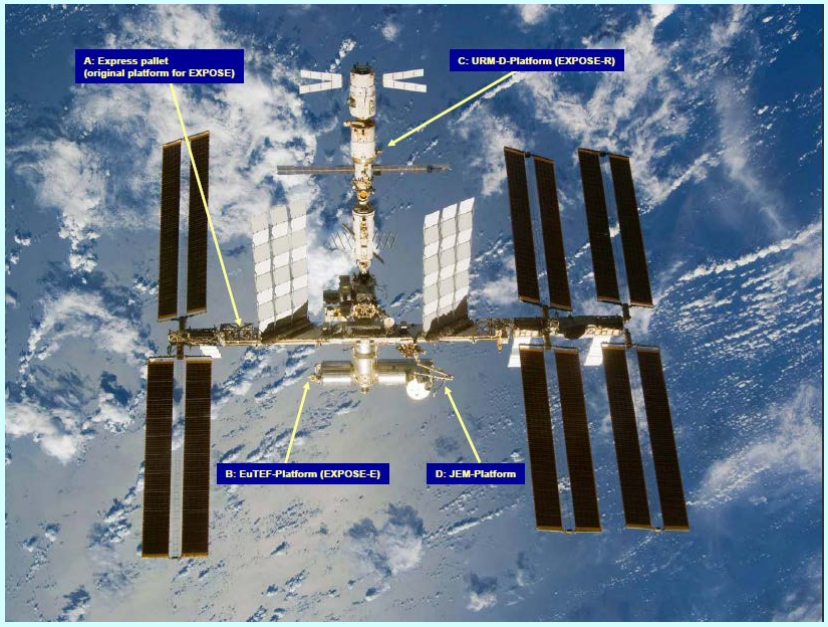


- **Glycine**
- **Alanine**
- **Valine**
- **Proline**
- **Serine**
- **Aspartic acid**

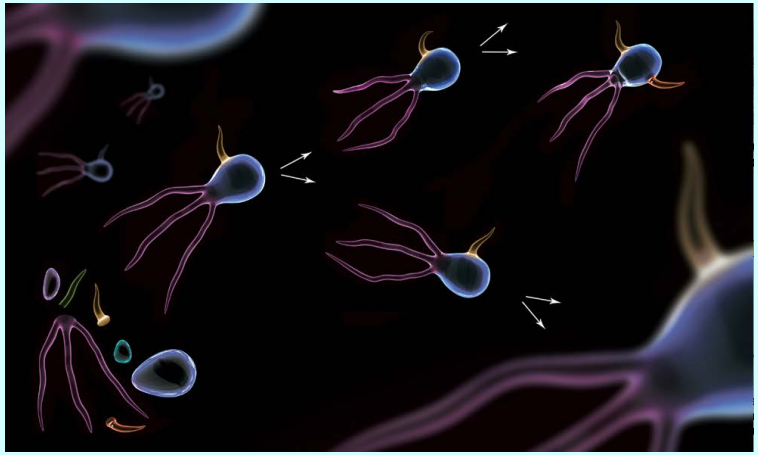


Amino acids were exposed in space: they travel safely in space if embedded in at least 5 microns of minerals.



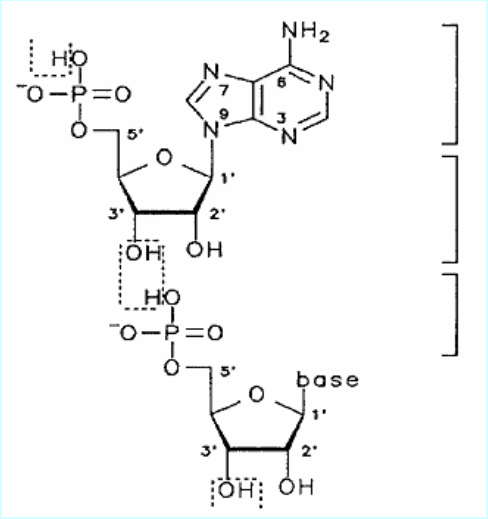


The origin of life
« Primordial soup »

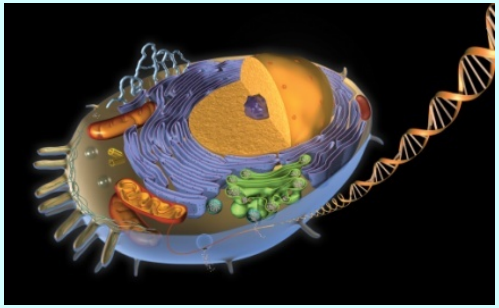


RNA world
Virus?

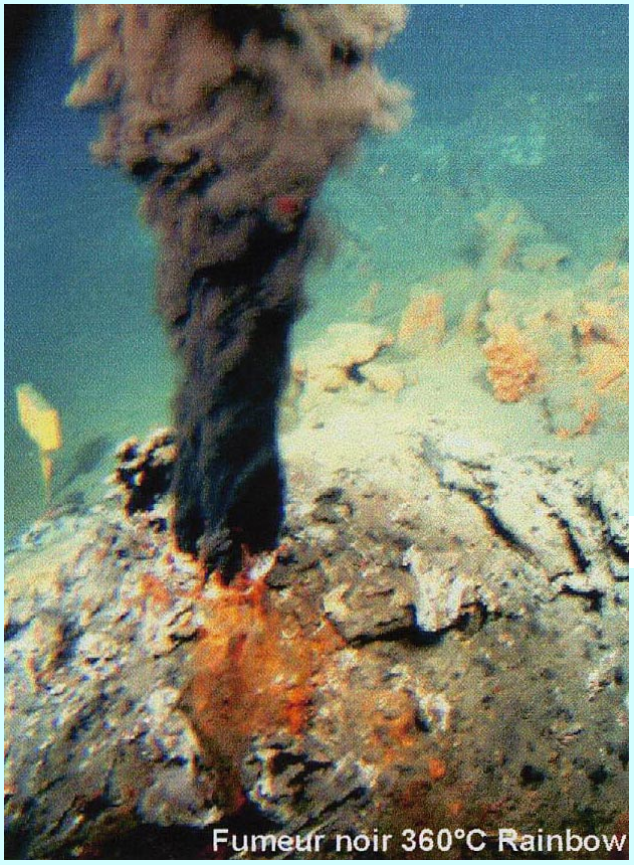
⇒

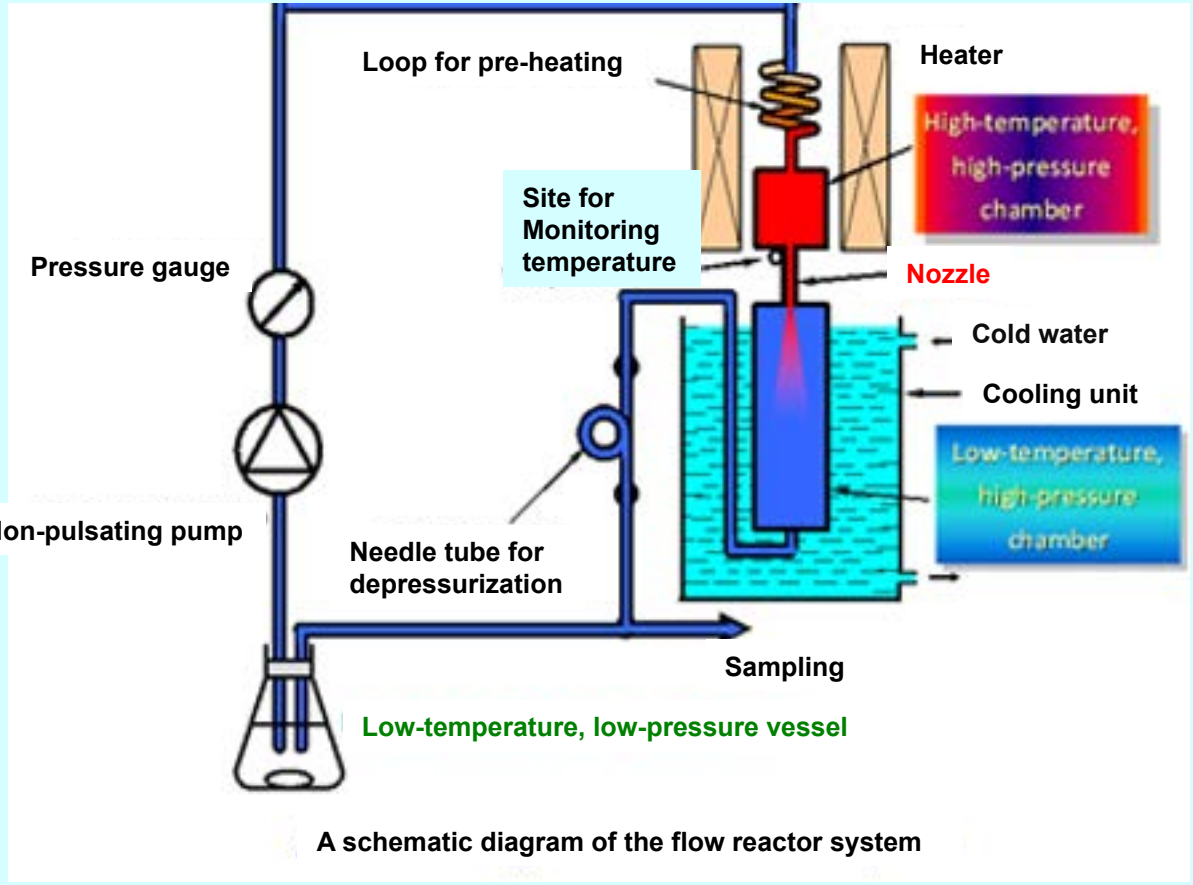


Cell with:
RNA
Proteins
Membranes



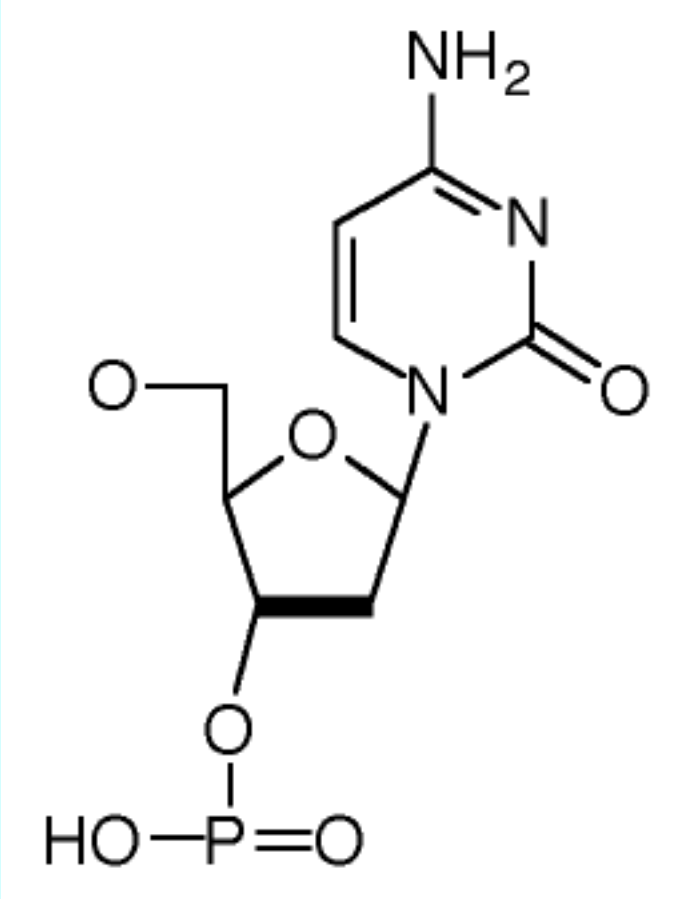
Polymerizing glycine by mimicking a hydrothermal system



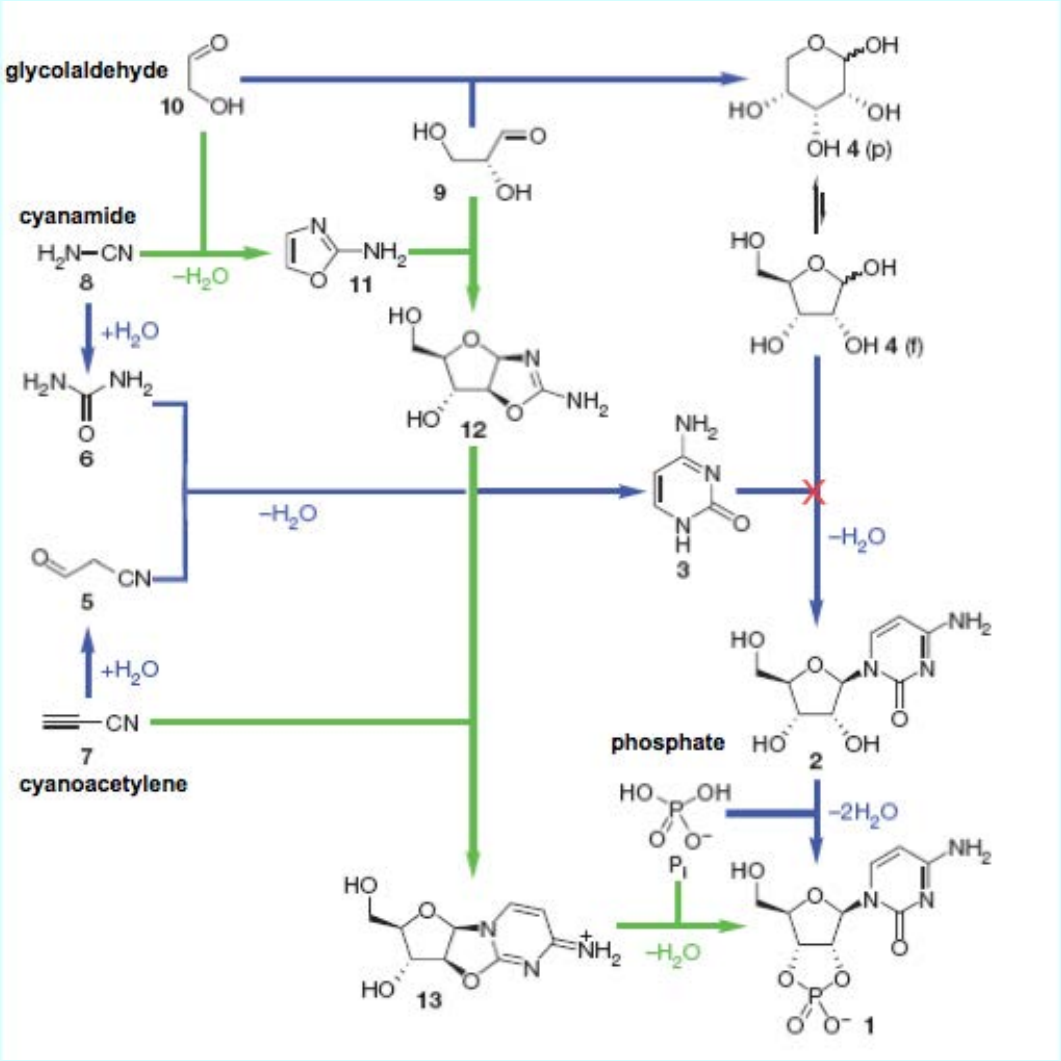


A schematic diagram of the flow reactor system

Bypassing free ribose and the nucleobases



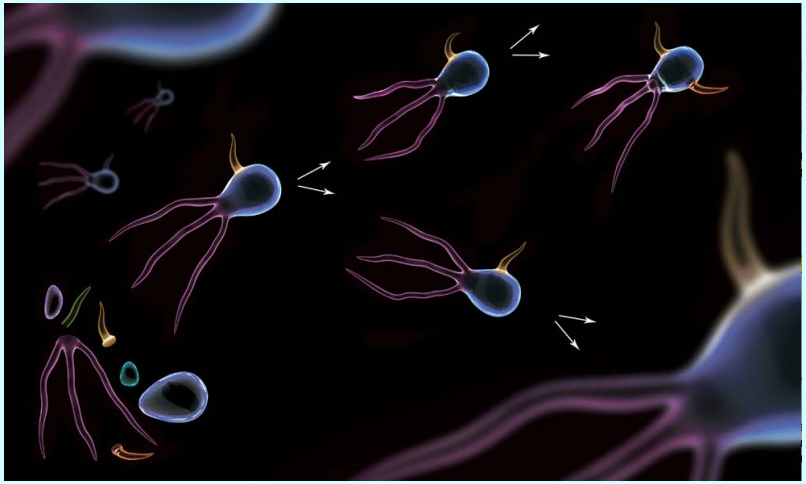
RNA nucleotide

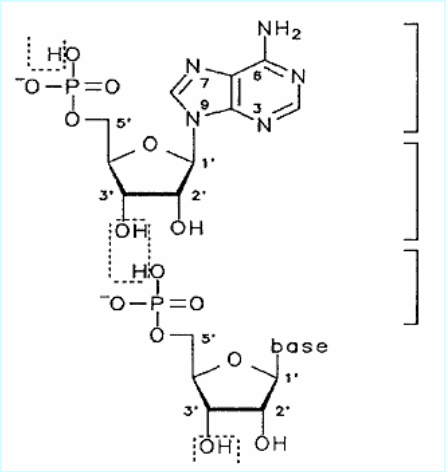


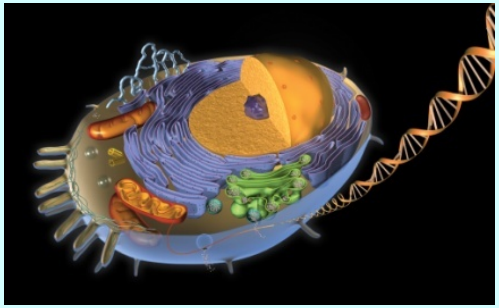
John Sutherland in 2009

The origin of life
Primordial soup hypothesis

CHONS + H_2O ⇒ **Chemical automata?** ⇒ **RNA Virus?** ⇒ **Cell with: RNA Proteins Membranes**





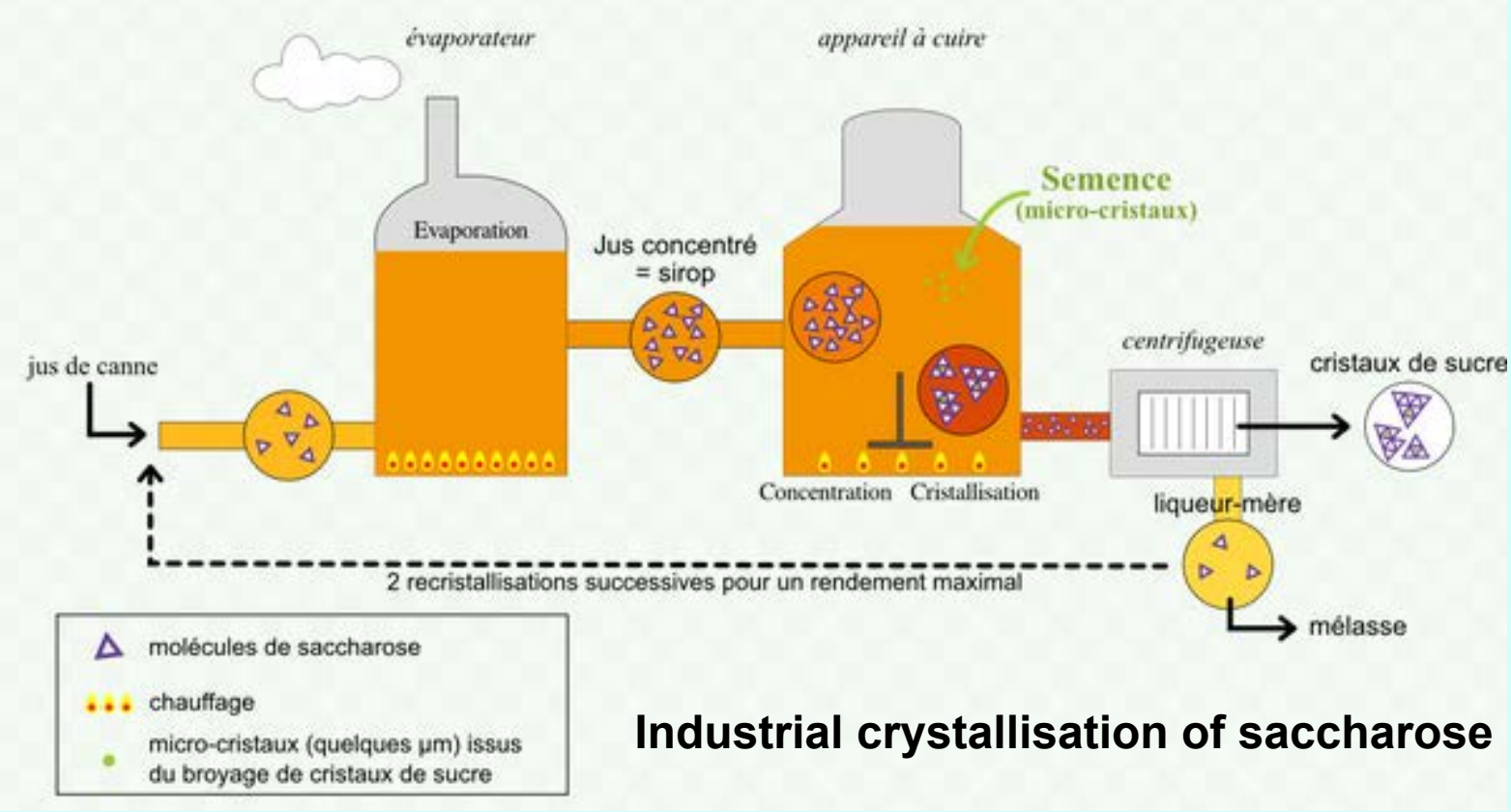


« Black » living entities fulfilling *a minima*

Self reproduction and evolution

Chemists are facing new dilemma:

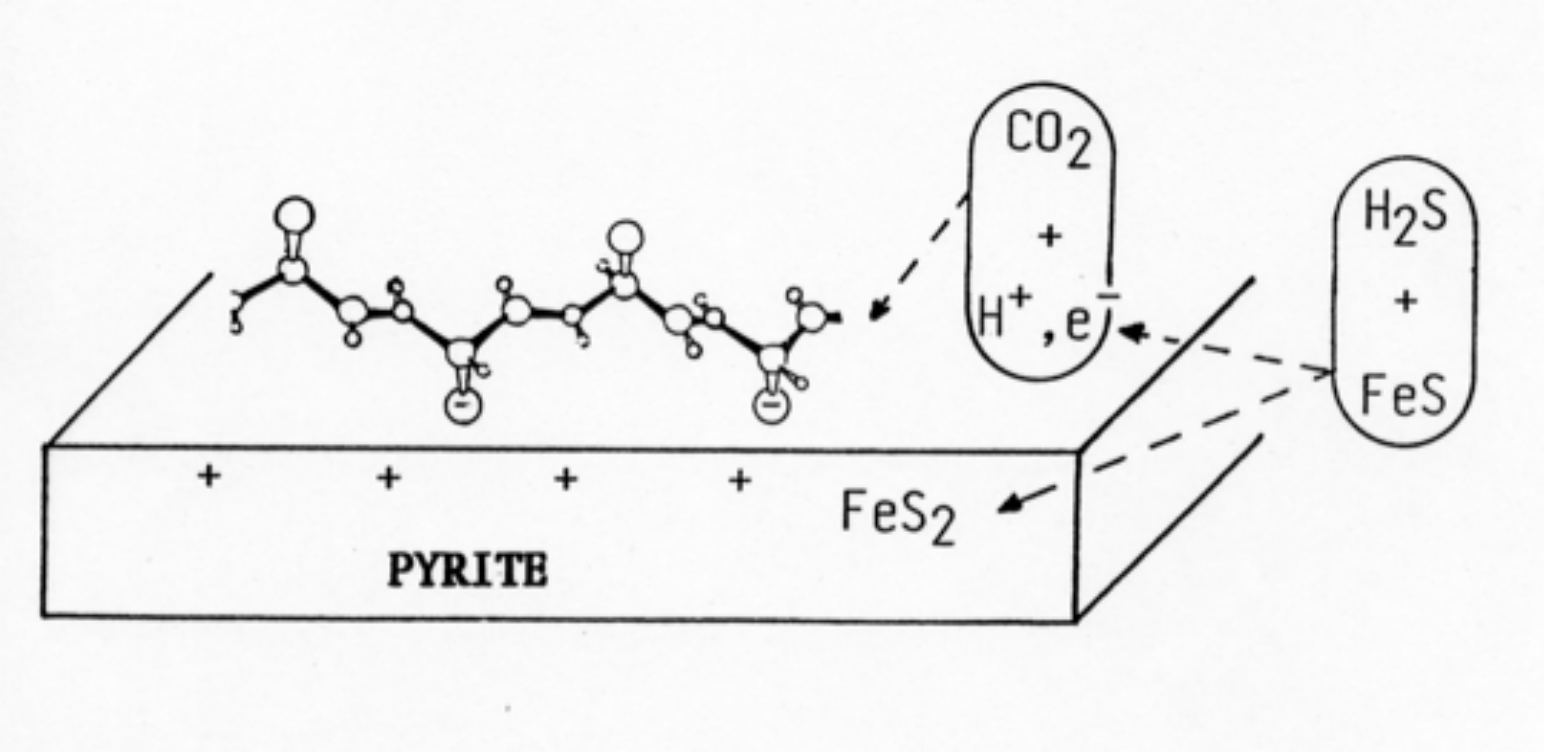
Singularity or ubiquity?
Should we consider :
- very specific local conditions ➔ few births seeding the whole primitive ocean?
- widespread conditions ➔ spontaneous births of life everywhere?



Industrial crystallisation of saccharose

Autotrophy instead of heterotrophy?

The «metabolism first» approach promoted by those who don' t like the soup



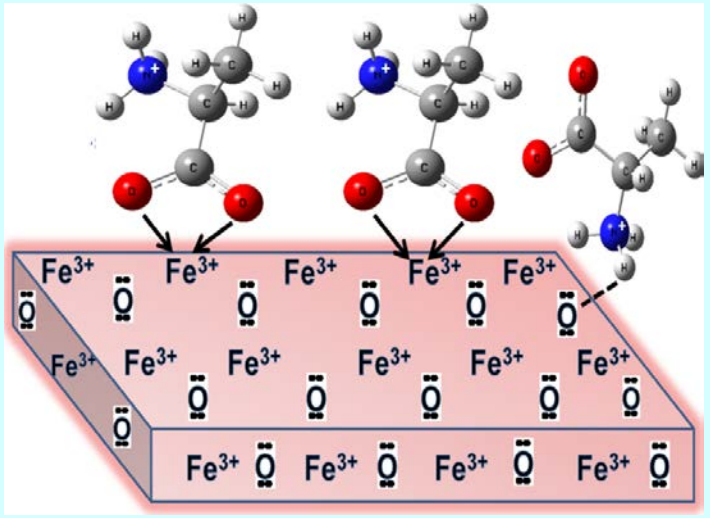
Step-by-step predictive chemistry or stochastic chemistry?

Step-by-step predictive chemistry ***versus*** **alchemist-type stochastic chemistry?**

i.e. to submit a maximum of prebiotic ingredients under prebiotic conditions and to let the system run for months…

Chemistry « on the rocks » ?

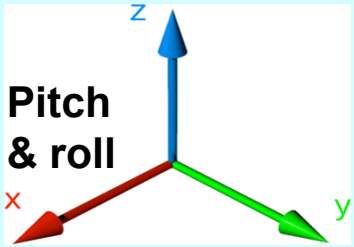
-Sélective adsorption
-Ionic interactions
-Reduced mobility
-Reduced hydrolysis



$\Delta G = \Delta H - T \cdot \Delta S$ ok if $\Delta G << 0$

Gibbs free energy — Enthalpy (Internal Energy) — Entropy (disorder)

	d° of freedom	ΔS	ΔH
Solution	6	<<0	~ 0
Surface	2	~ 0	~ 0



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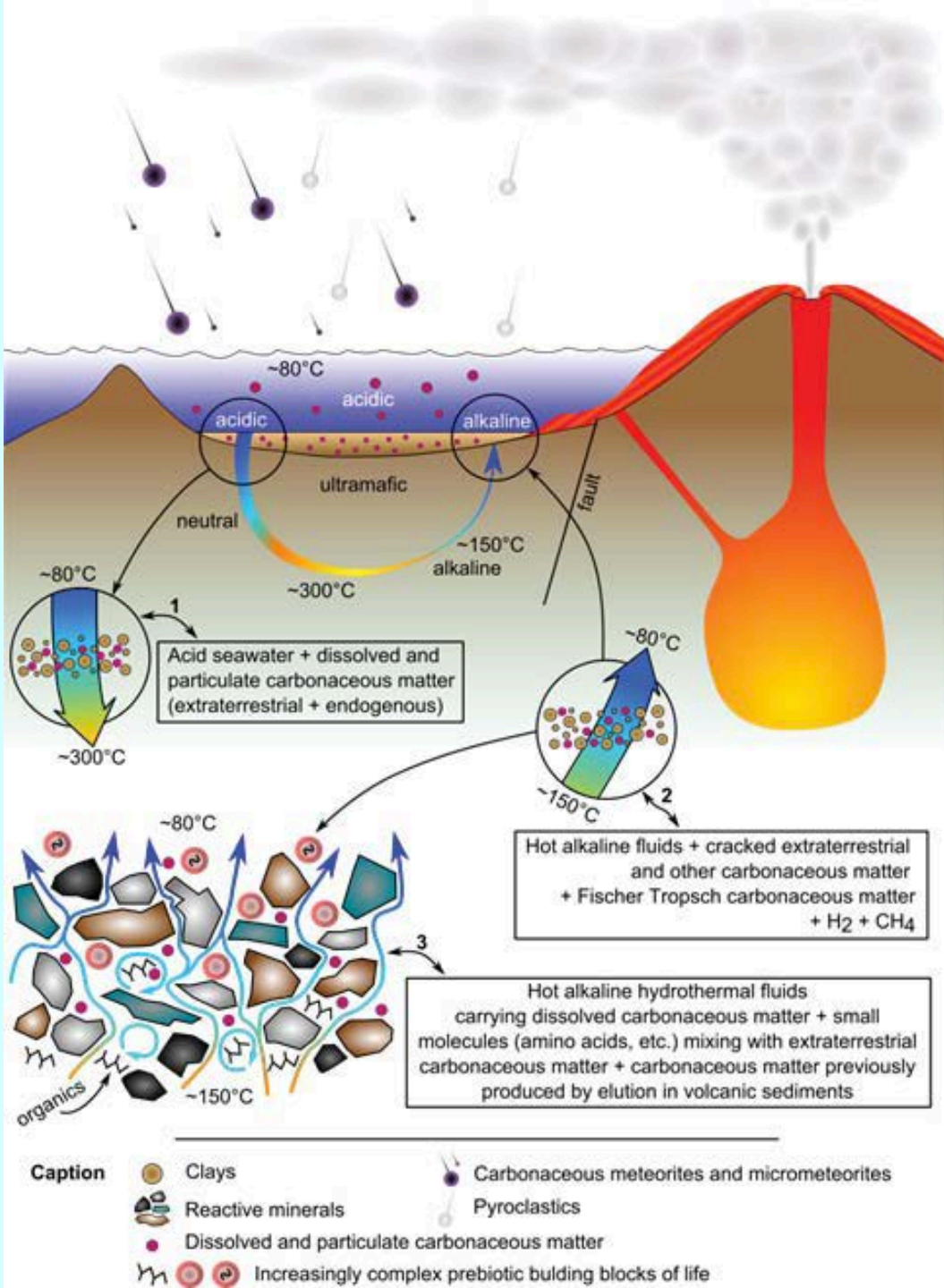
Chemistry with rocks?

A new approach developped in Orléans:
Stochastic chemistry in a geochemical context as realistic as possble
→ open chemical system far from equilibrium permeating through sediments in a hydrothermal environment



Simple or awfully complex?

The discovery of a second genesis would support simplicity.

Where could we find liquid water and carbon chemistry?

Mars?

Europa?

Titan?

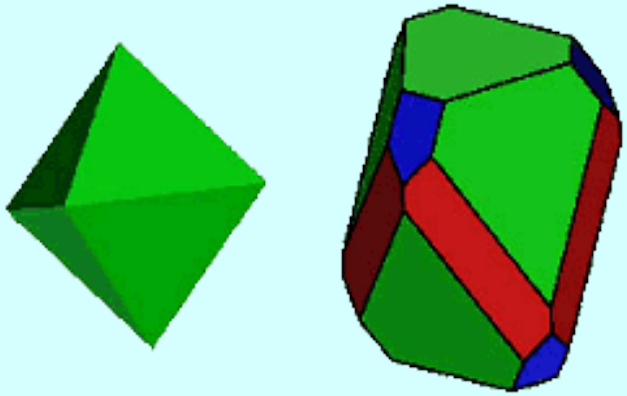
Enceladus?

Exoplanets?

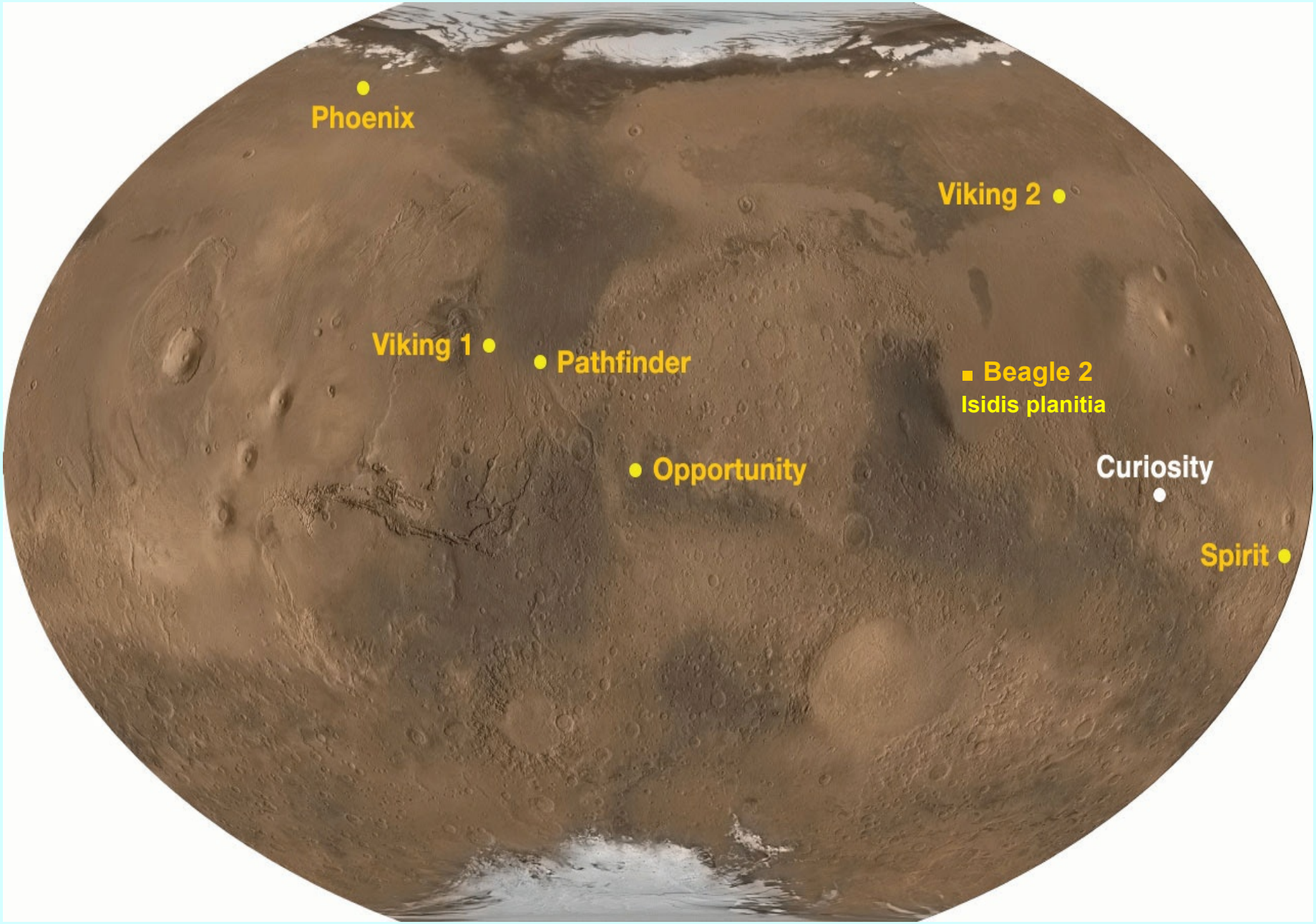
Mars is our first target

The red planet hosted liquid water ⇒ it had therefore an atmosphere
⇒ it inherited organic-containing micrometeorites

96 meteorites are accepted as Martian, including the famous ALH84001

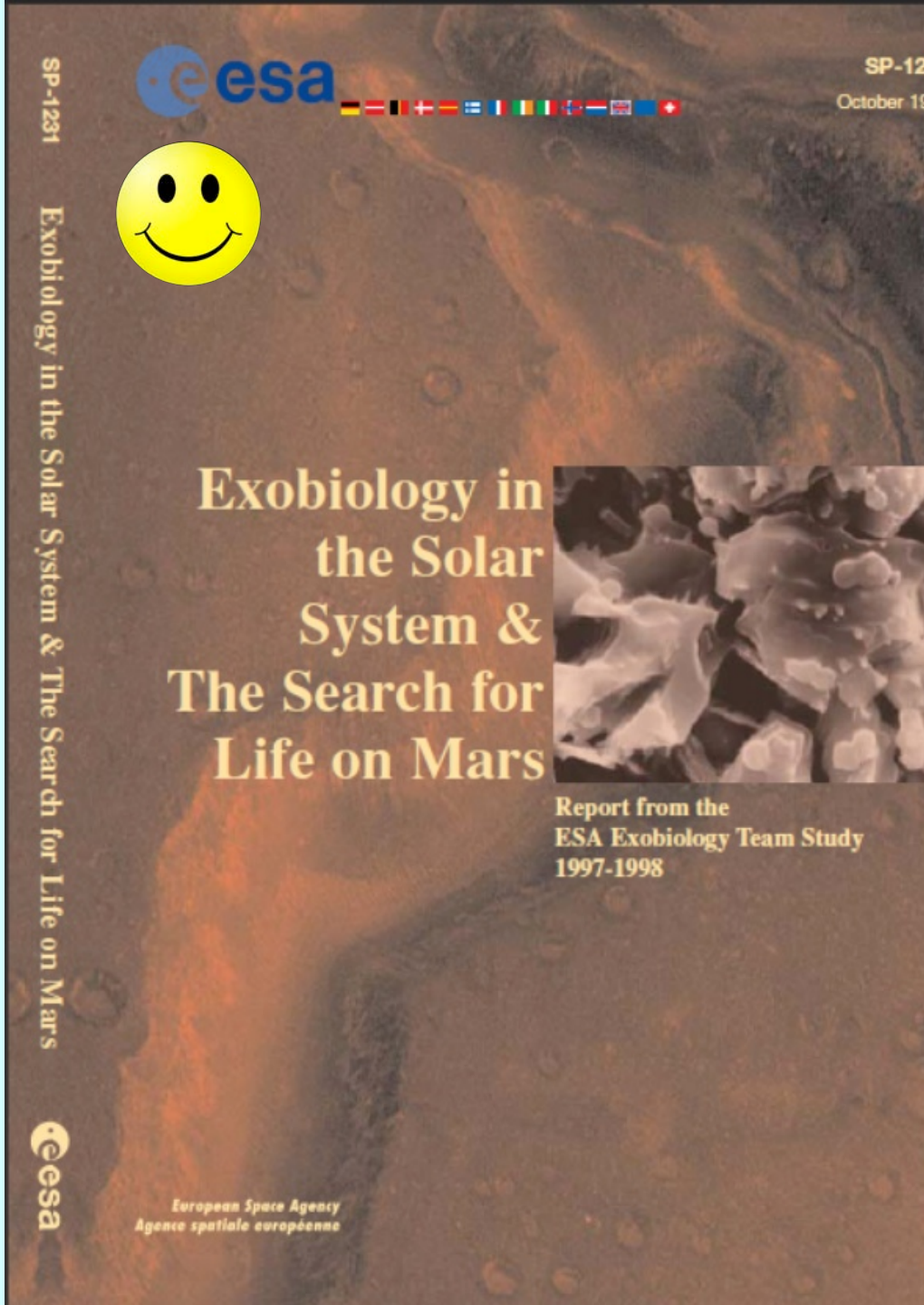



In 1976, Viking did not find organics at the Martian surface

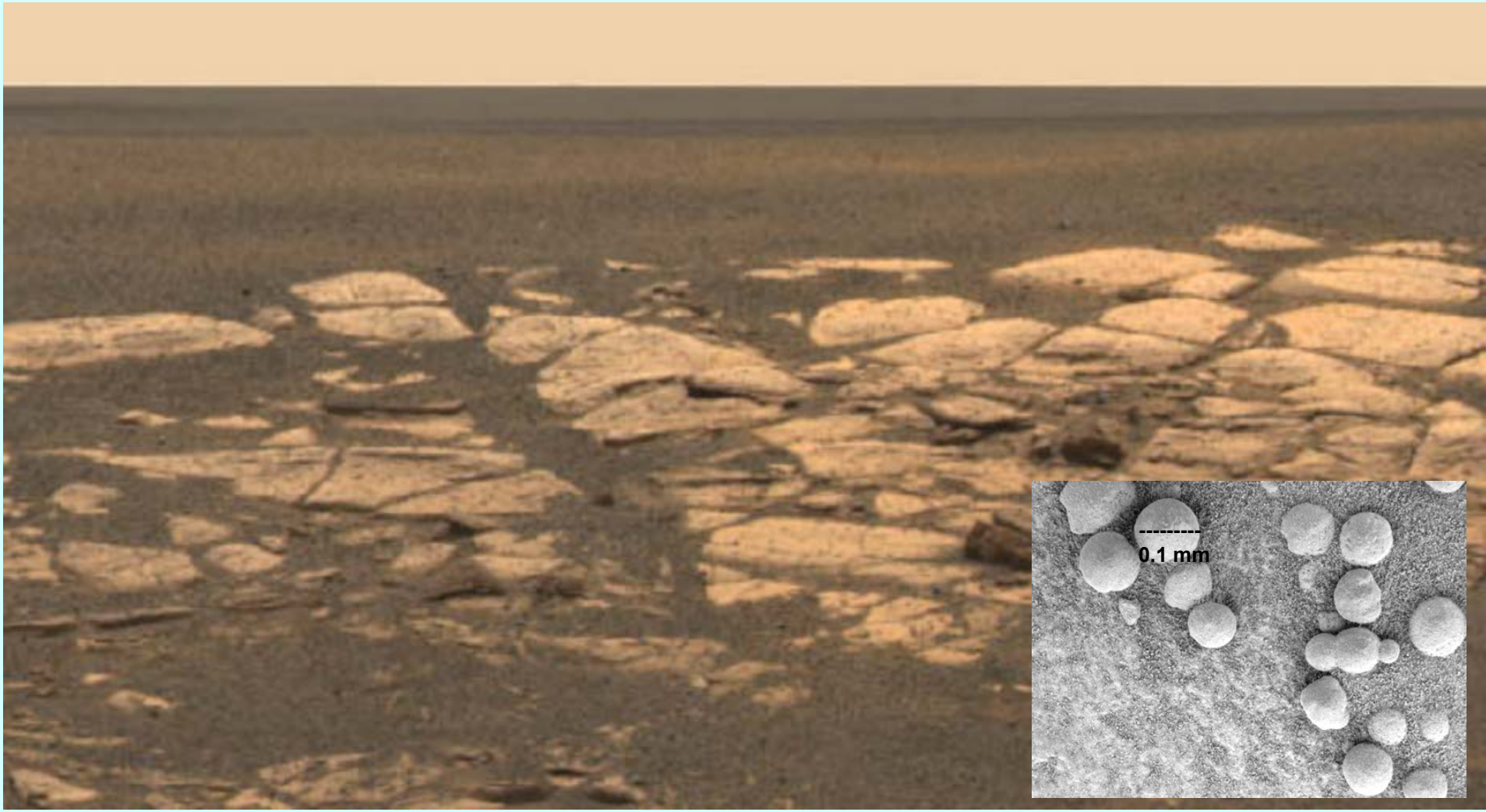

Phoenix
Viking 2
Viking 1
Pathfinder
Beagle 2
Isidis planitia
Opportunity
Curiosity
Spirit

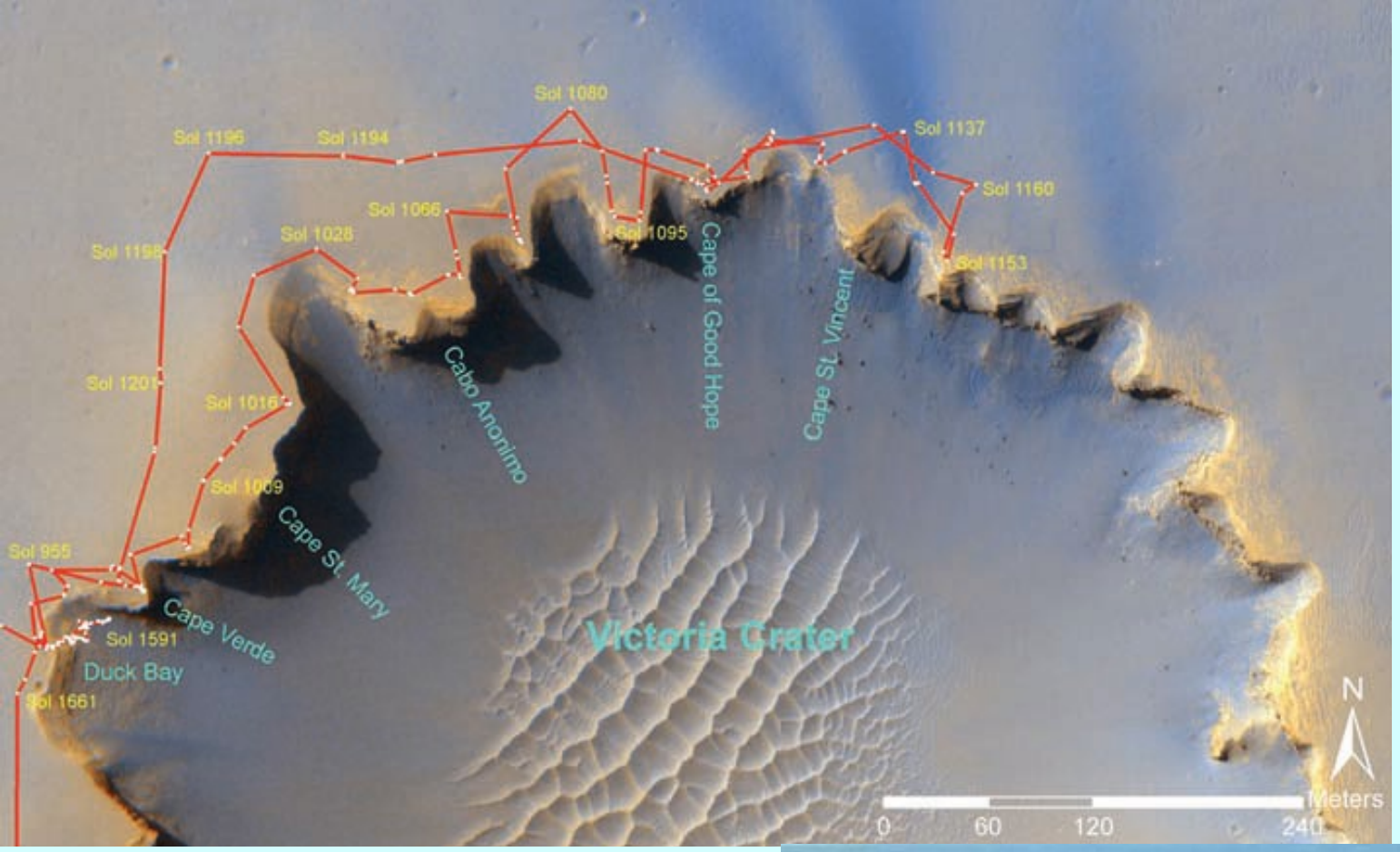
Orléans contribution

1997: head of the ESA Exobiology Science Team.
2001: Agreement for a lander on Mars Express. Head of the adjunct science team of Beagle 2.
2003: crash of Beagle 2



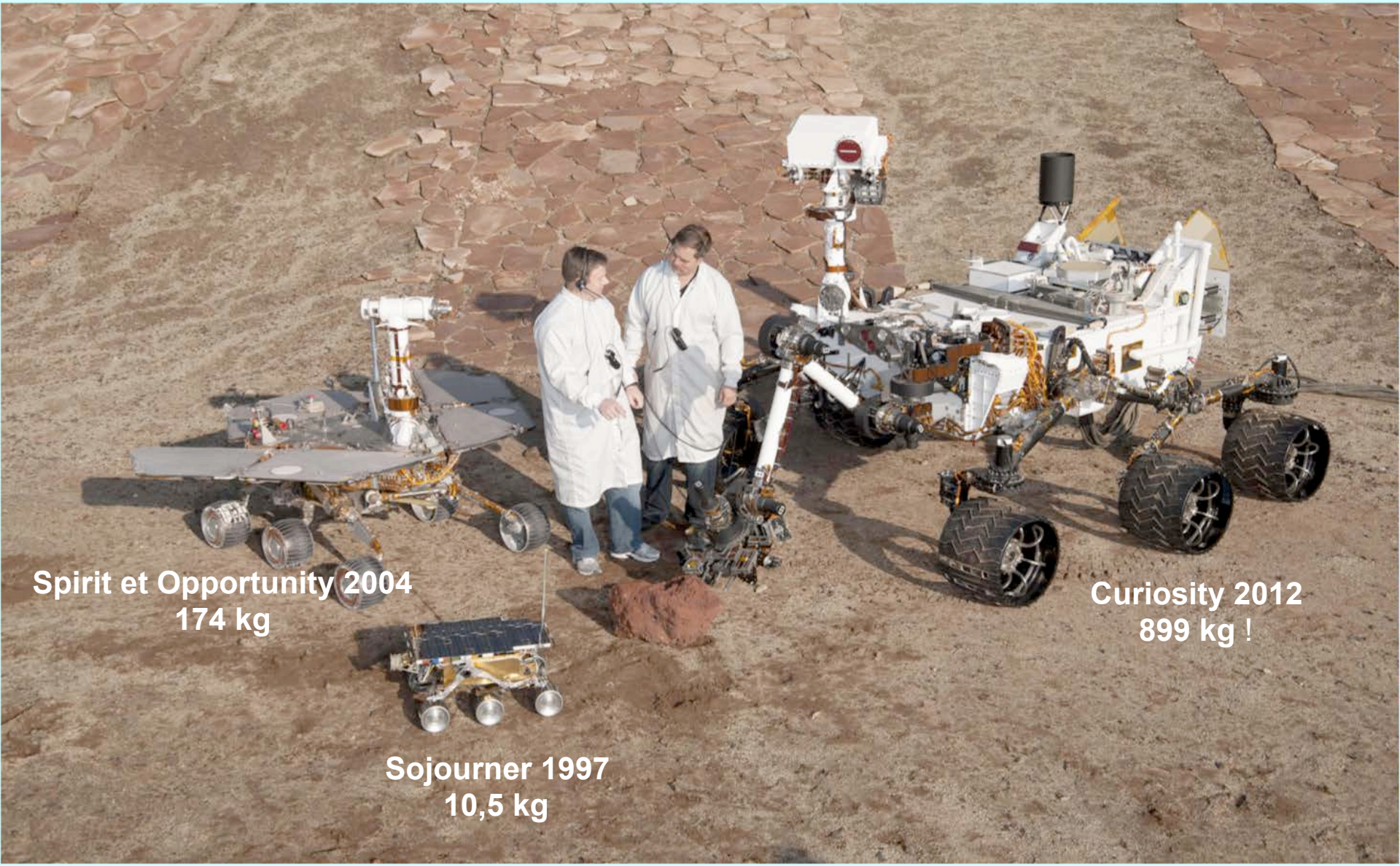
Opportunity landed at Meridiani Planum on the 25th of January 2004 for 3 months Investigations. It Is still operating!





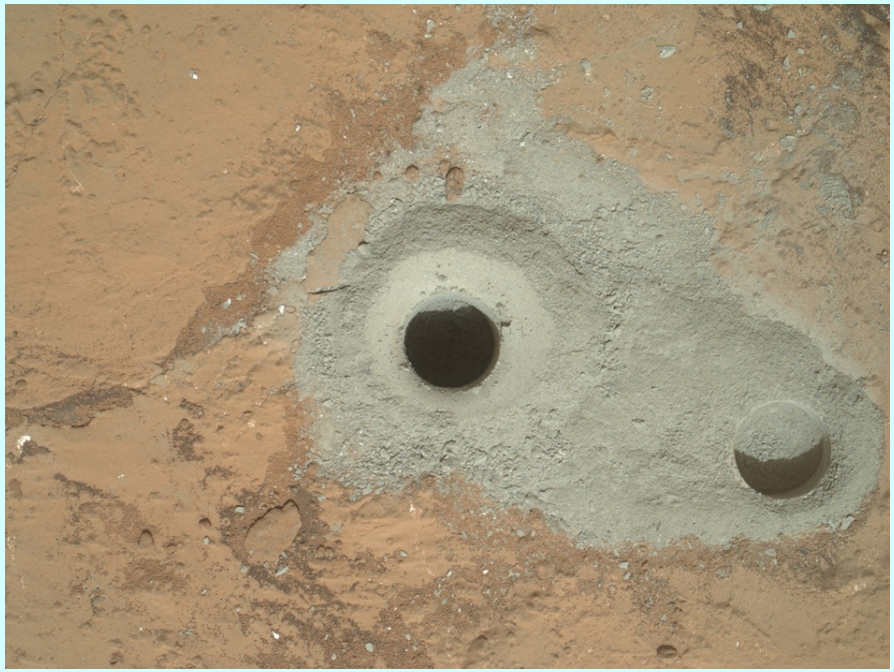
Hematite 'blueberries' are present in Victoria Crater cliff
⇒ ancient sea

Curiosity, 2011
Search for traces of life, organics and oxidants


Spirit et Opportunity 2004
174 kg
Sojourner 1997
10,5 kg
Curiosity 2012
899 kg !

Curiosity, 2011

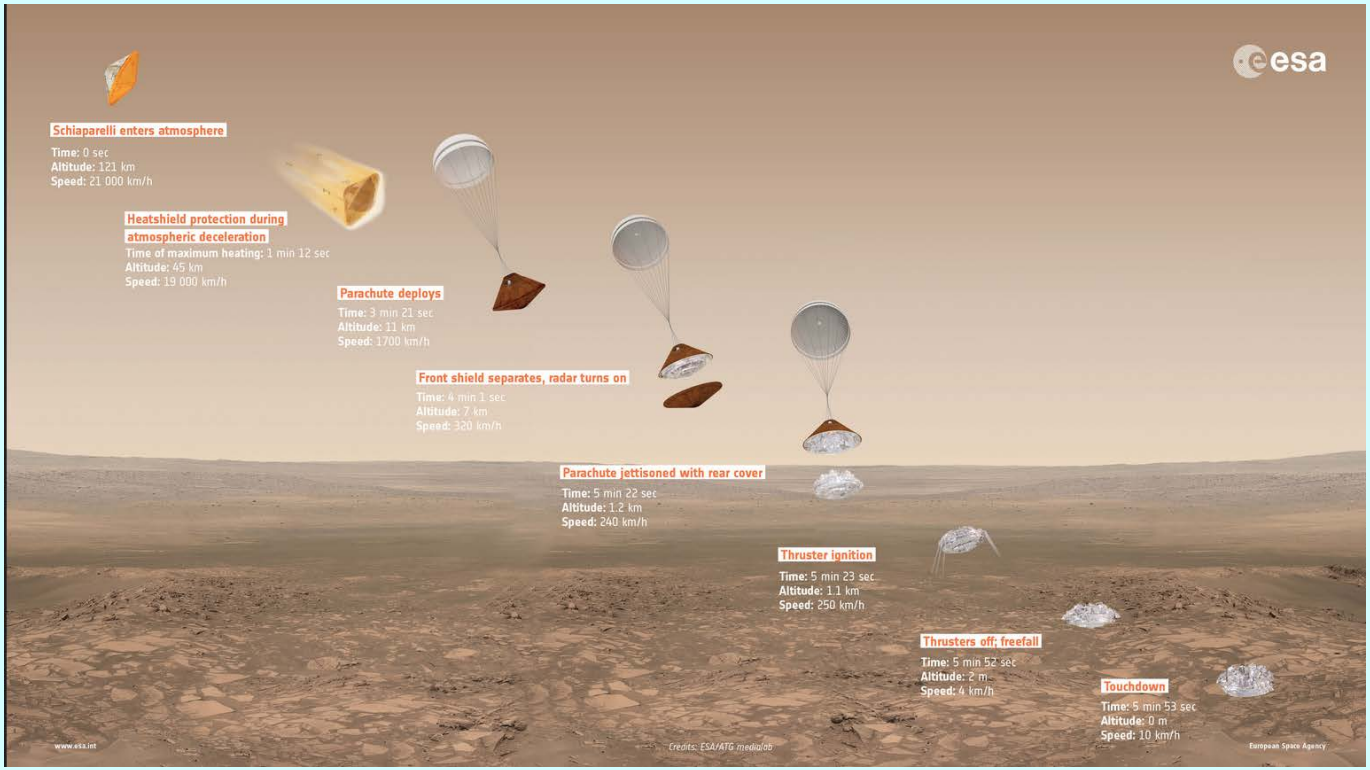
- Ancient fresh water lake (clays and gypsum)
- presence of chemical elements able to generate life (carbon, hydrogène, oxygen, phosphate, sulfur) but no prebiotic organic molecules detected so far.



The two step ESA EXOMARS mission, a joint endeavour between ESA and Roscosmos

2016: launch on March 14 of the Orbiteur TGO (methane, telecommunication relay) with the demonstration lander Schiaparelli at *Meridiana Planum.*

October 19: crash of Schiaparelli



For less than 1 second, a dysfunction of the Inertial Measurement Unit indicated a negative altitude!

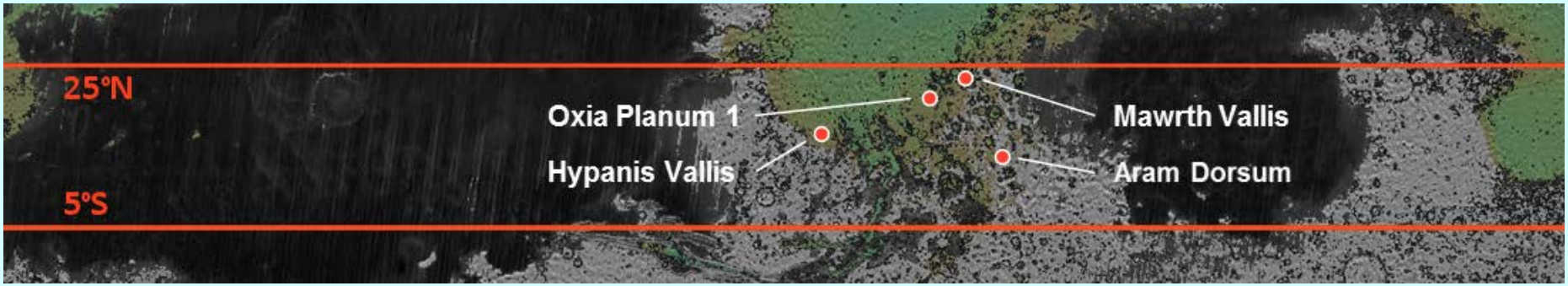
EXOMARS

2020

Rover to search for traces of life with a drill (2 m) and a complete suite of instruments « Pasteur ». Russia will provide the launcher.

Contribution of Orléans

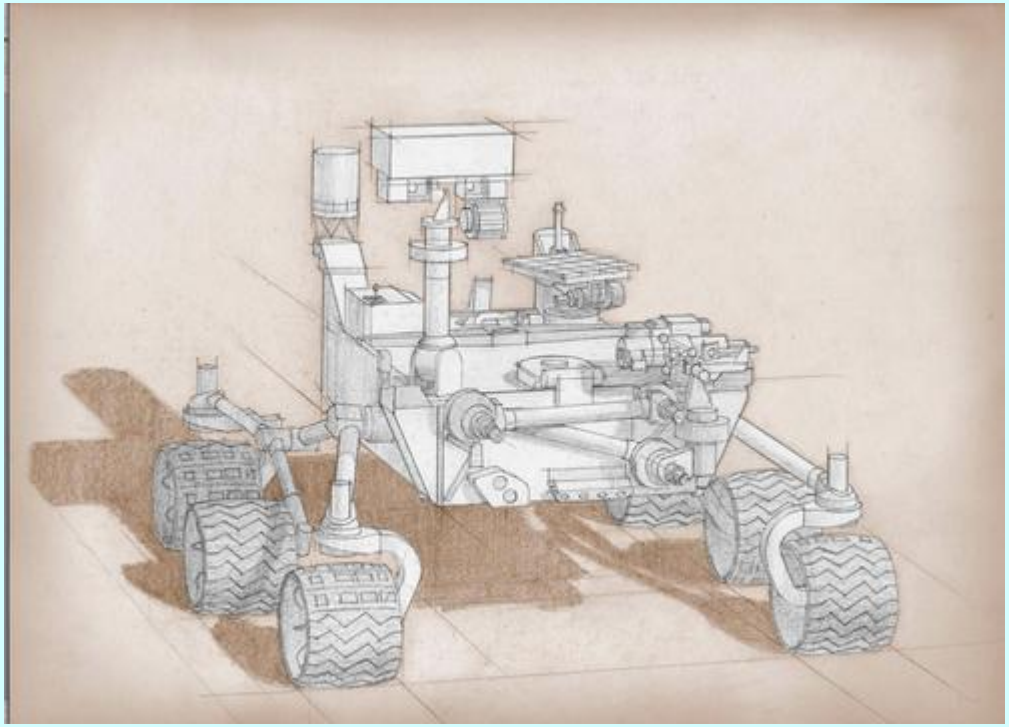
Close-UP Imager (CLUPI), a camera system designed to acquire high-resolution, colour, close-up images of outcrops, rocks, soils, drill fines and drill core samples. The visual information obtained by CLUPI will be similar to what a geologist would get using a hand lens ... if they were on Mars!

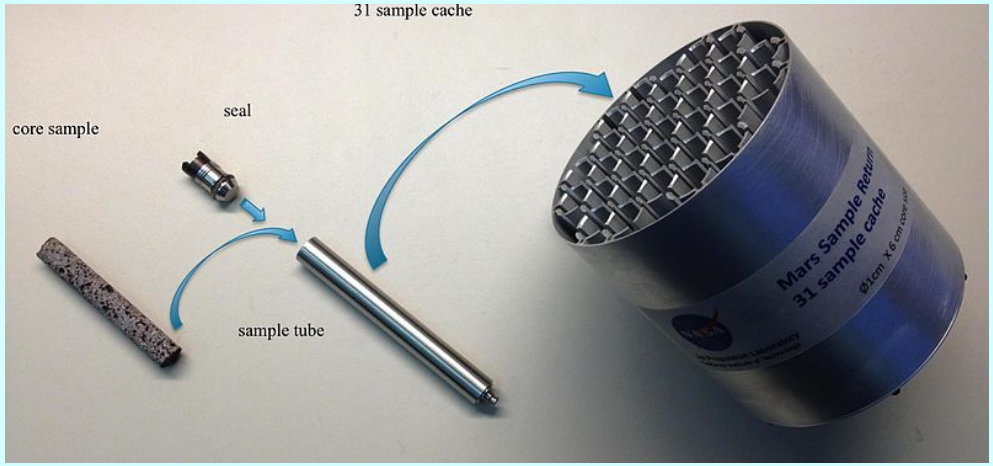


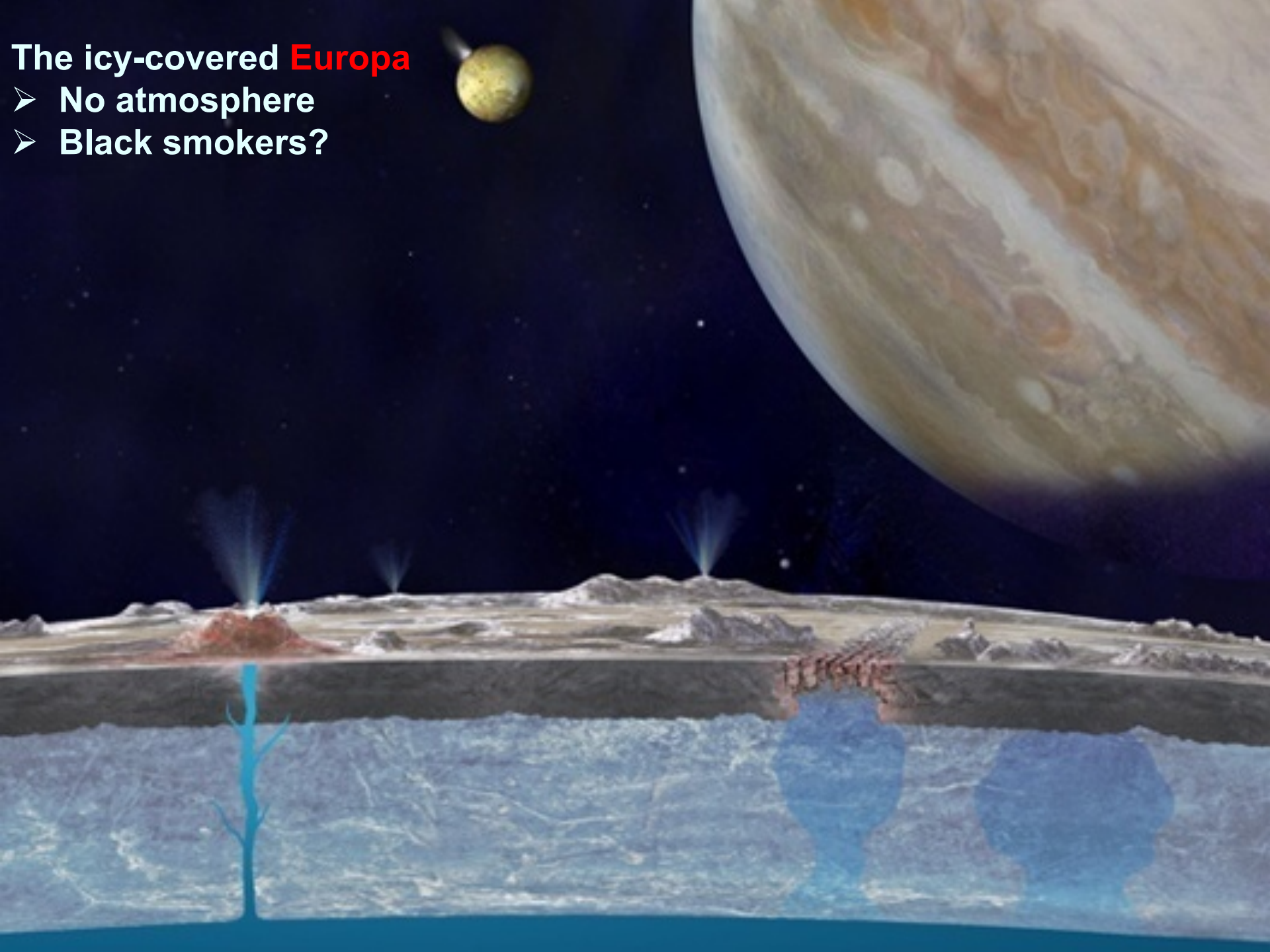
The US Mars 2020 mission

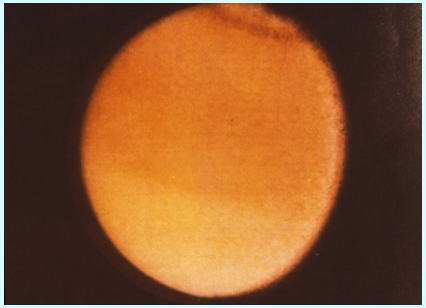
To:

- **search for traces of life**
- **collect samples for a subsequent Mars sample return**
- **test a protection technology for a manned mission (Martian dust)**
- **test how to collect carbon dioxide as a source of oxygen and fuel for the return rocket)**



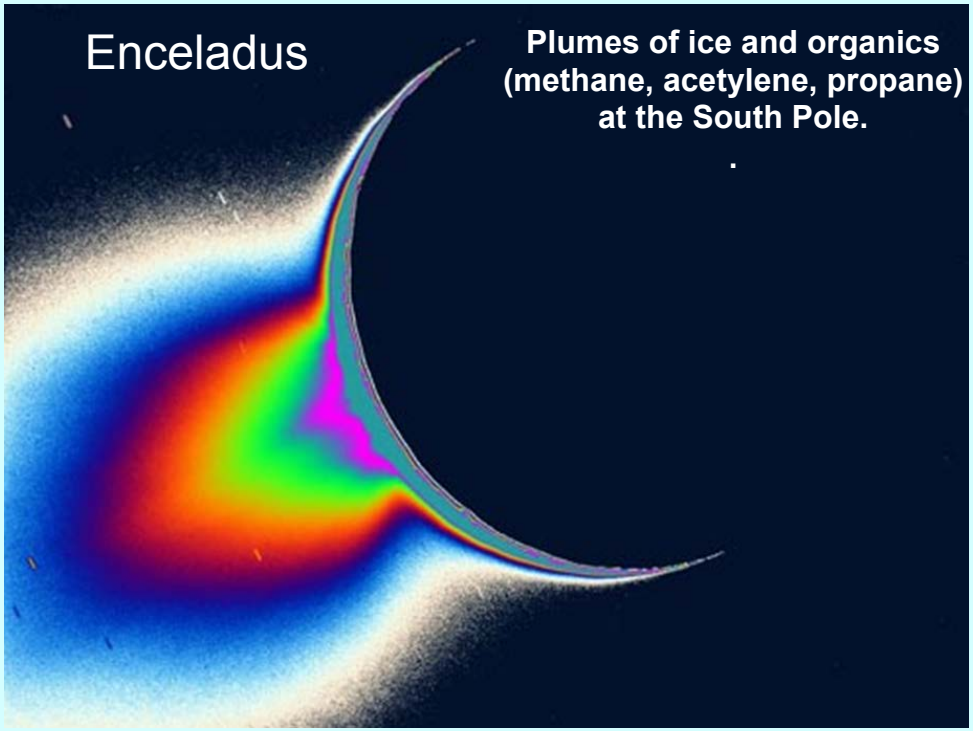


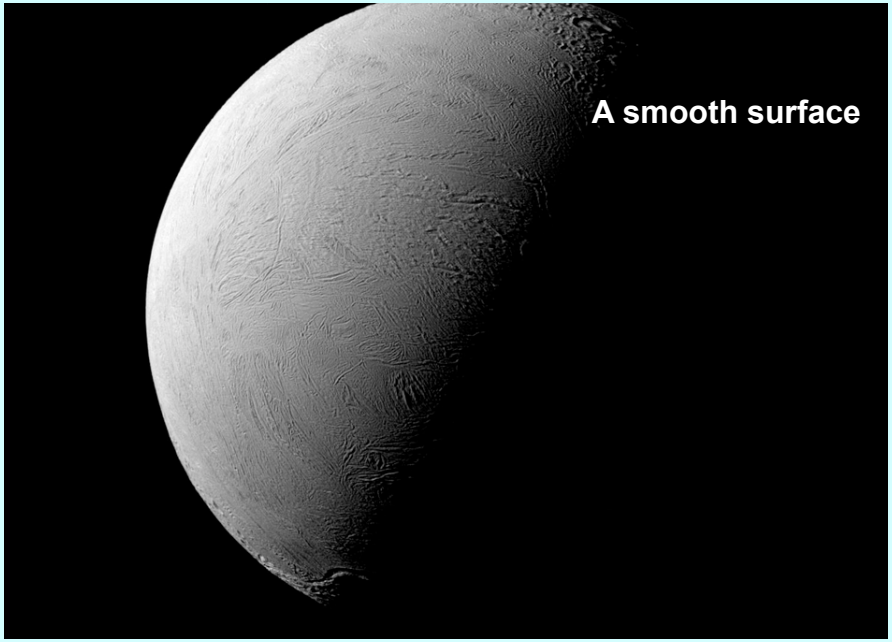

The icy-covered Europa
No atmosphere
Black smokers?



Titan:

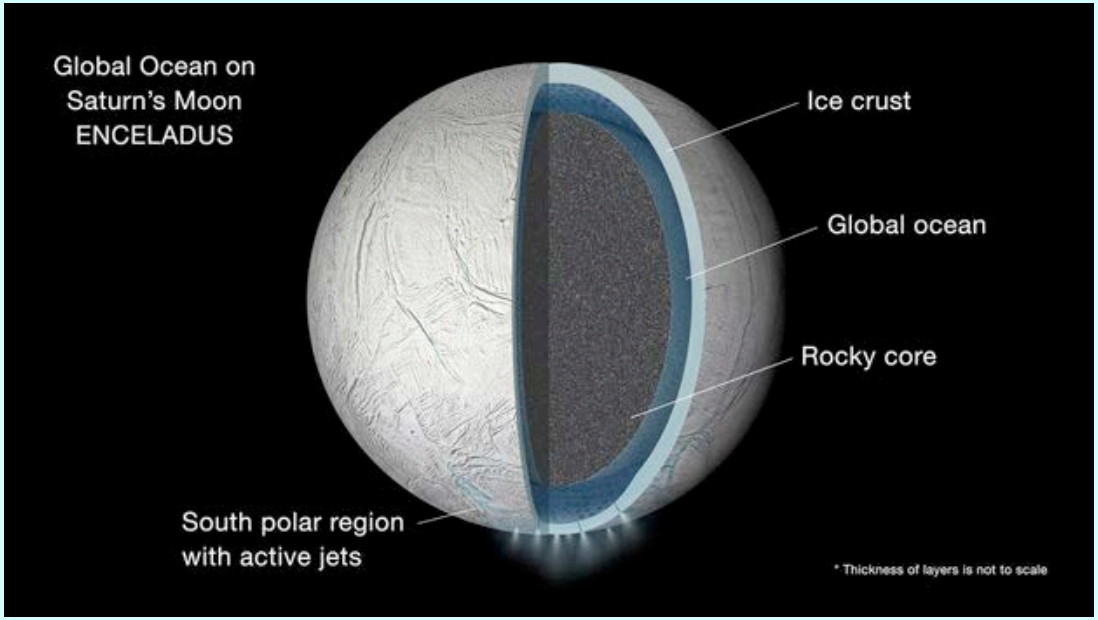
- **Very active atmospheric organic chemistry**
- **Too cold for liquid water**

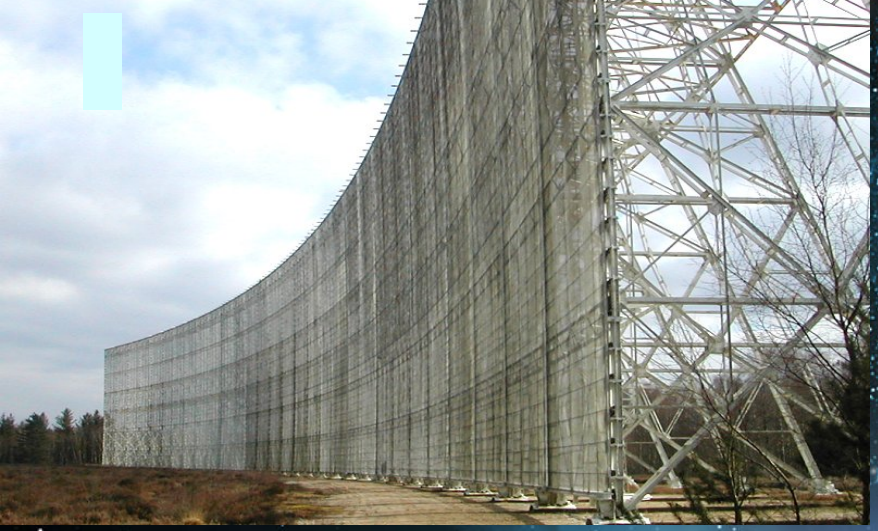




September 2015

Analyses from the Cassini probe suggest the presence of an ocean beneath the icy carapace.

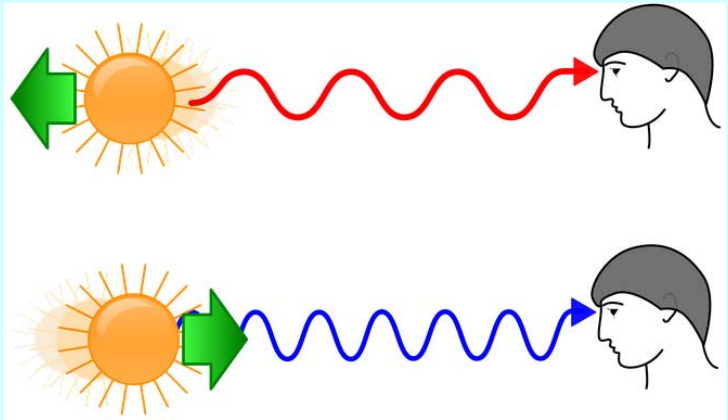




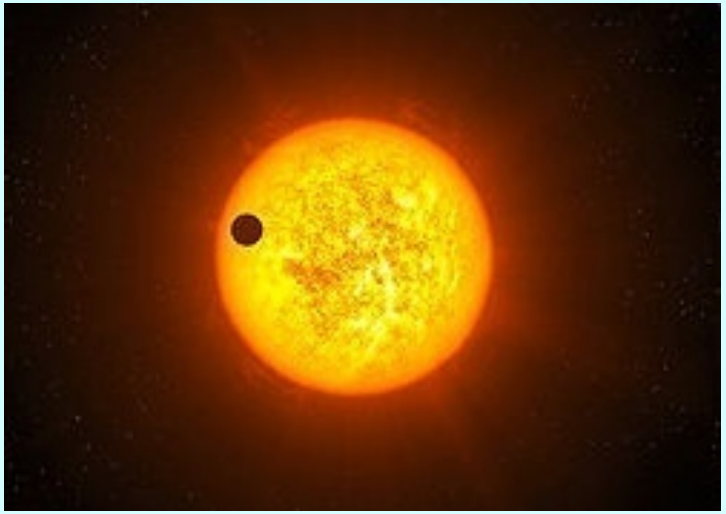
Buckminster fullerène C60
HCN, HCHO... $HC_{10}CN$

Organic chemistry is universal…
Over 110 organic molecules detected by radioastronomy (only 11 silicon ones)
Stellar planetary systems are universal
So are comets

3660 explanets have been detected so far, using mainly 2 methods:
- Radial velocity

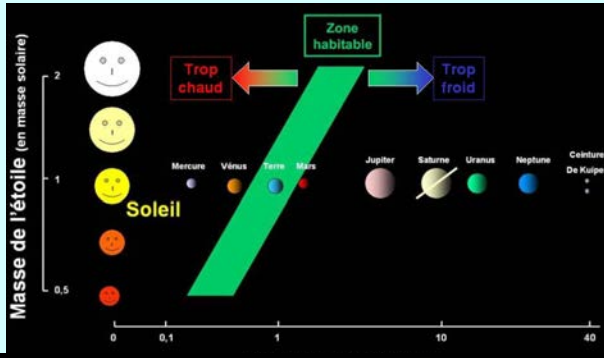


. Transit
(space telescopes COROT et Kepler)



Three new concepts are under study:
- STARE low-cost small satellite concept for the very nearest stellar systems,
- NEAT two formation-flying satellites to survey the 200 nearest Sun-like stars
- THEIA, a single-unit telescope designed to survey the 50 nearest stars.

Among the 3660 exoplanets detected, 44 are considered as habitable. Here are the 13 nearest of home. Do they host life?



Potentially Habitable Exoplanets

Ranked by Distance from Earth (light years)

PHL

[4.2 ly] Proxima Cen b

[13 ly] Kapteyn b*

[22 ly] GJ 667 C c

[22 ly] GJ 667 C e*

[22 ly] GJ 667 C f*

[39 ly] TRAPPIST-1 e

[39 ly] TRAPPIST-1 f

[39 ly] TRAPPIST-1 g

NEW

[41 ly] LHS 1140 b

[561 ly] Kepler-186 f

[770 ly] Kepler-1229 b

[1115 ly] Kepler-442 b

[1200 ly] Kepler-62 f

Earth

Mars

Neptune

Jupiter

Artistic representations. Earth, Mars, Jupiter, and Neptune for scale. Distance from Earth is between brackets. Planet candidates indicated with asterisks.

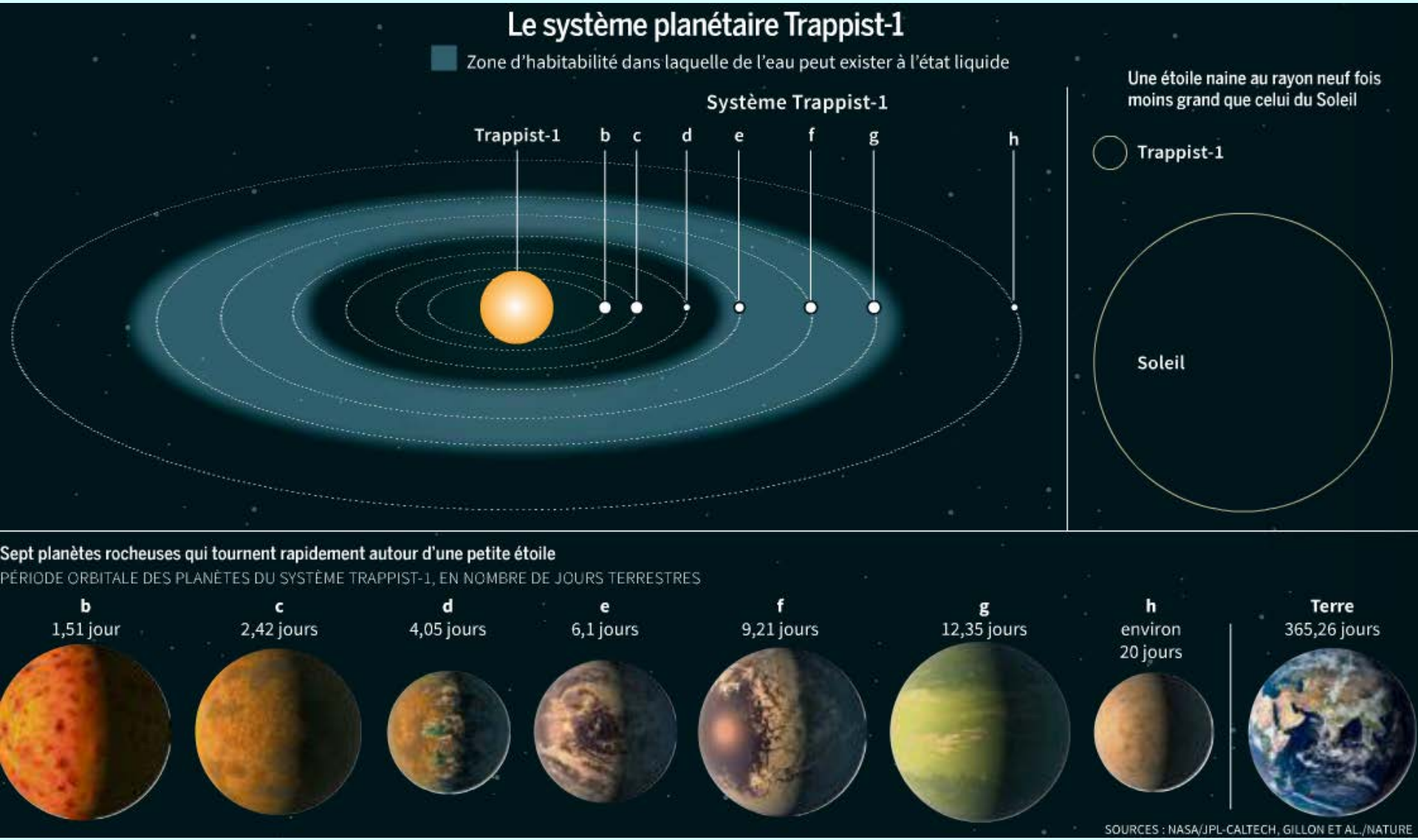
CREDIT: PHL @ UPR Arecibo (phl.upr.edu) May 11, 2017

A living exoplanet in our backyard?

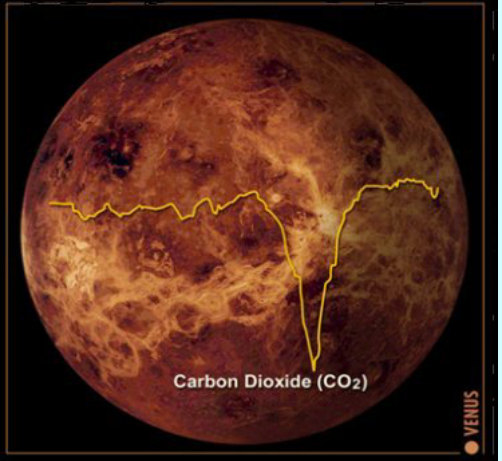
In August 2016, discovery of an exoplanet orbiting Proxima Centauri, the nearest star, a red dwarf at « only » 4.2 light-years (40 000 billion kilometers).
1.3 time terrestrial mass
A « classical » space mission would take...20,000 years.
Stephen Hawking and Mark Zuckerberg (Facebook) are developing the Starshot Project: a nanocraft pushed by a laser and the solar wind should reach its target and send pictures in 2061…

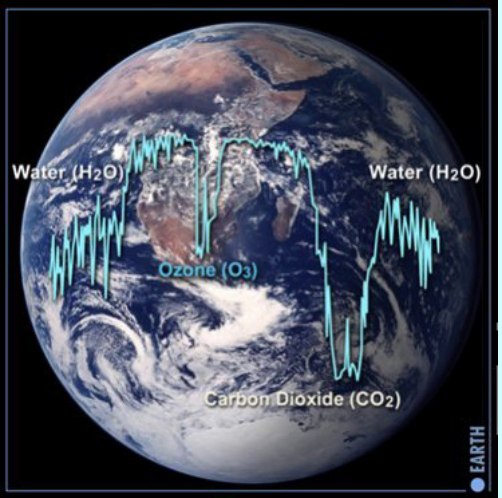
February 22, 2017

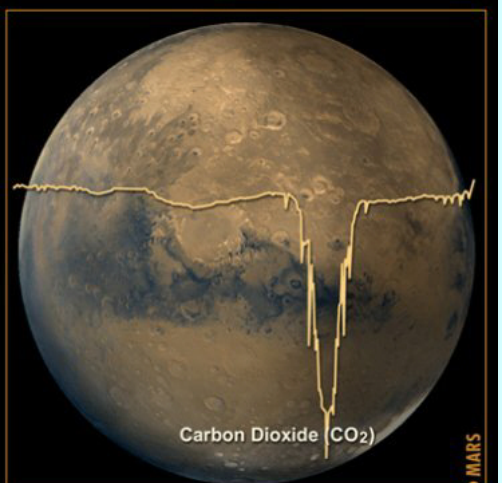
Detection of 7 Earth-size planets orbiting red dwarf TRAPPIST at 39 light-years. Three of them are in the habitable zone allowing the presence of liquid water.



Densité 5,52 (3,93)

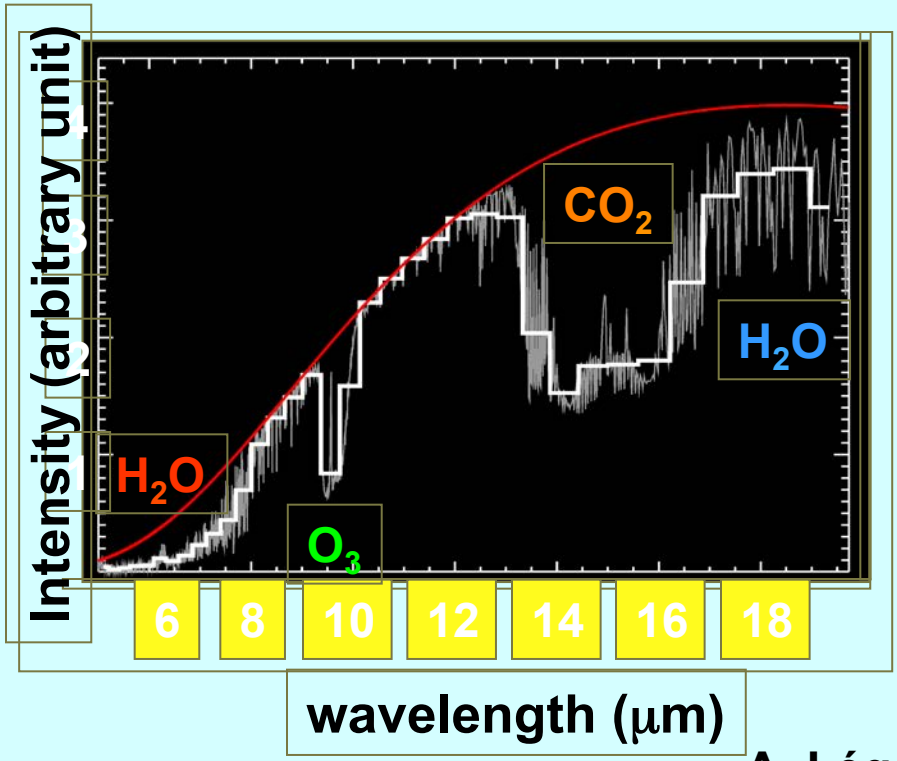




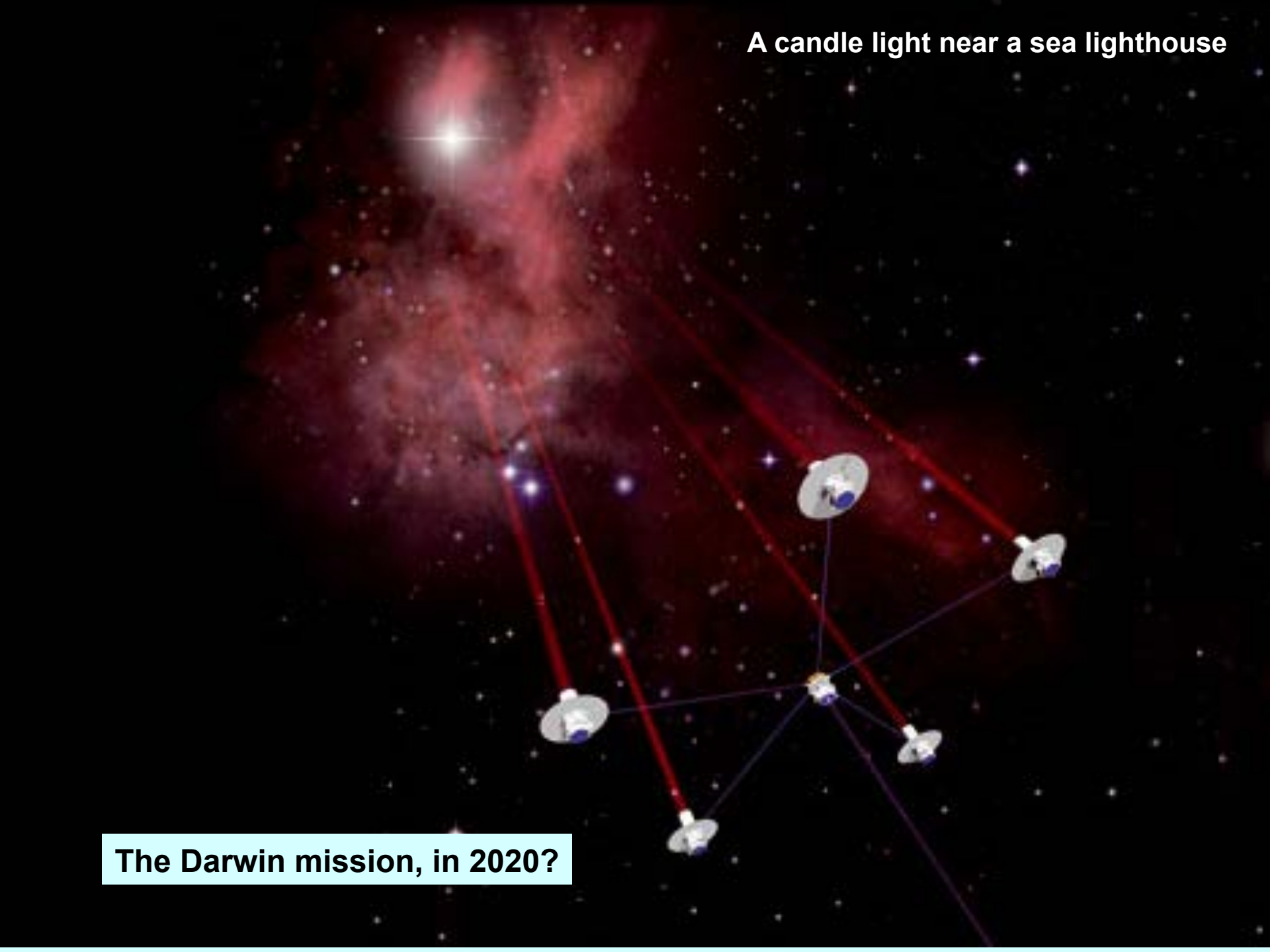


Biomarkers in the atmosphere of exoplanets

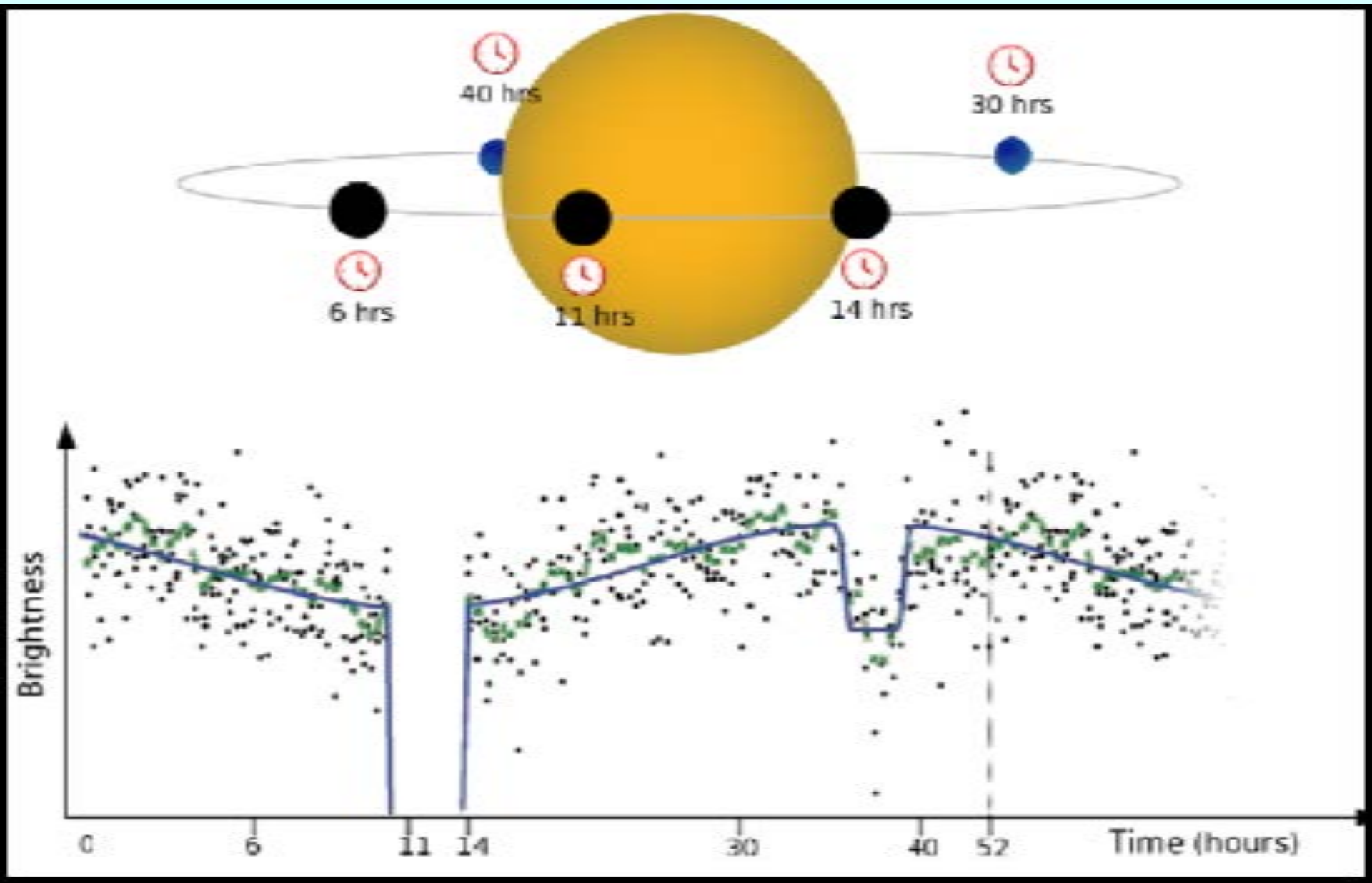
$$\{CO_2 + H_2O + O_3\}$$



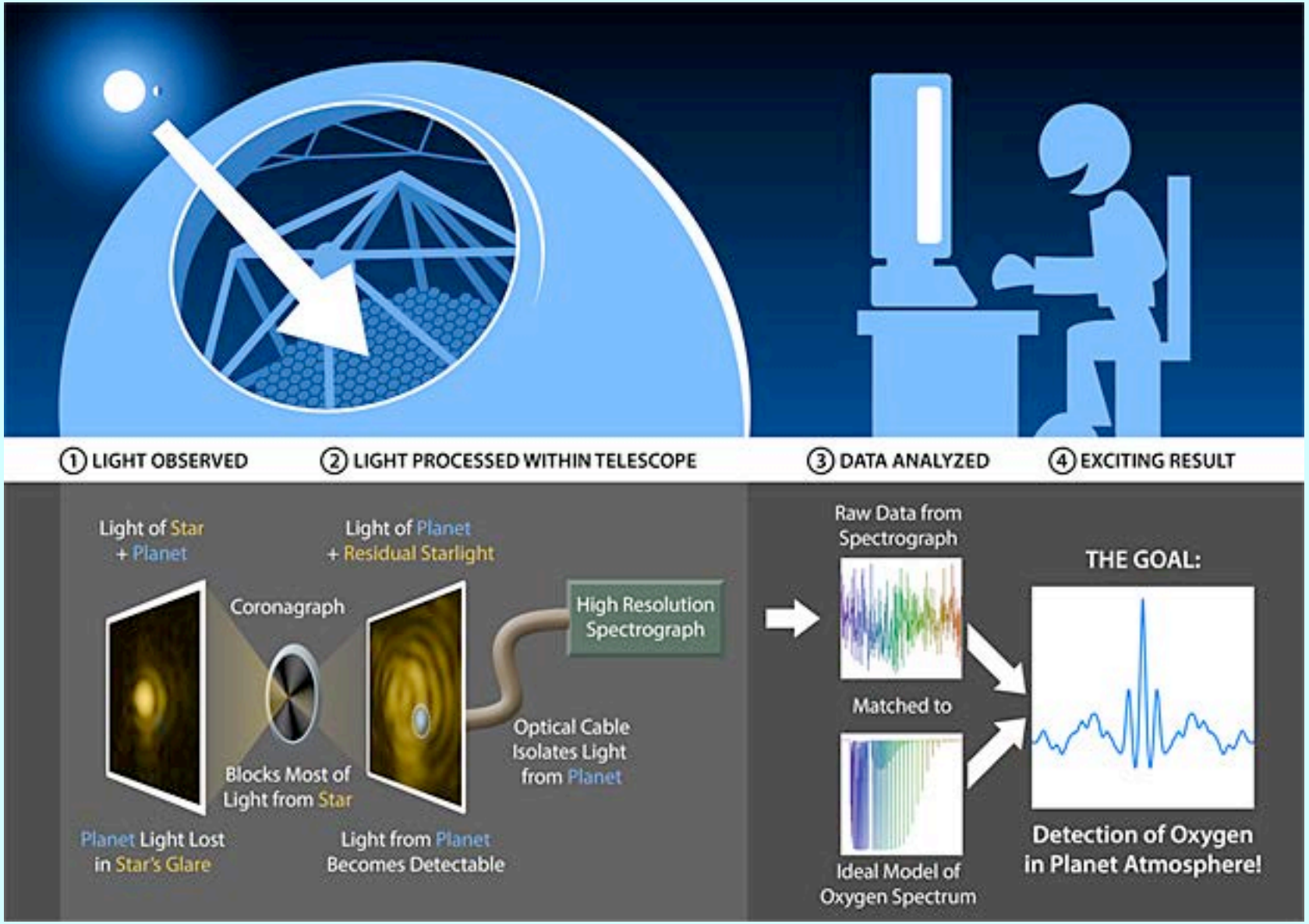
A. Léger


A candle light near a sea lighthouse
The Darwin mission, in 2020?

Spectroscopy of a planetary atmosphere during its primary transit



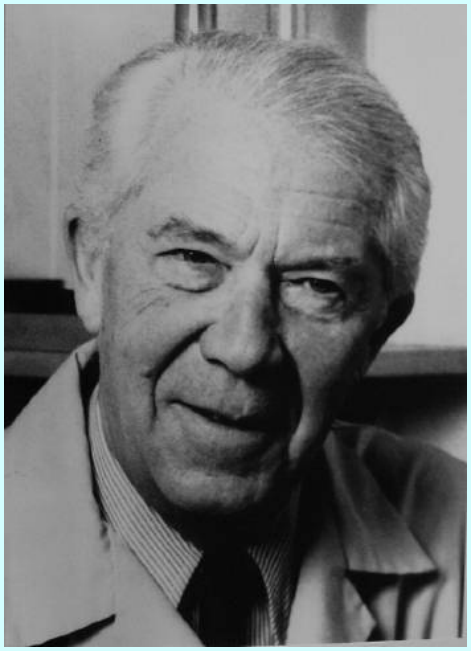
April 2017
High dispersion coronography should allow to detect oxygen as a bioisignature with the 30 m telescope operational in 2020



Christian de Duve (1917- 2013) Nobel Laureate in 1974

« "I knew the joy of learning, the almost voluptuous pleasure to understand,…", … »

A l'écoute du vivant, p. 362 (2002)

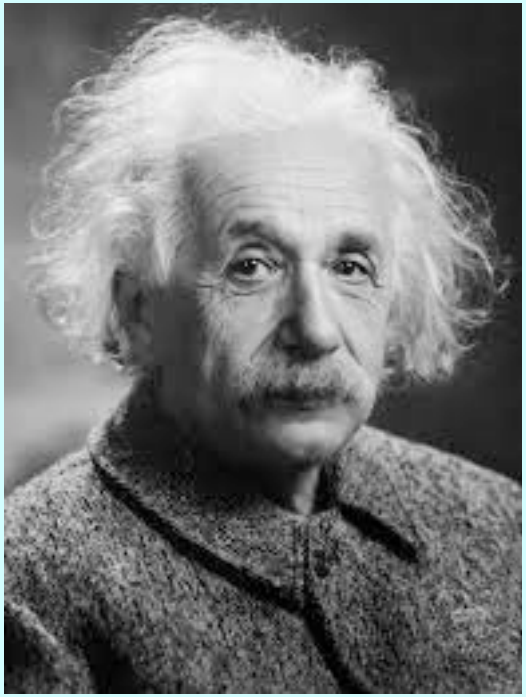


Seneca (4 av. JC → 65) wrote :

«The most beautiful discoveries would cease to please me if I were to keep them for me »

Wichtig ist, daß man nicht aufhört zu fragen

It is important to never cease asking questions



Mars is a better fossil repository than the Earth:
- **little plate tectonics**
- **little rain**
- **no oxygen**

Earth handicaps:
- **plate tectonics**
- **UV <2 Ga**
- **rain**
- **«biological» oxygen >2 Ga**