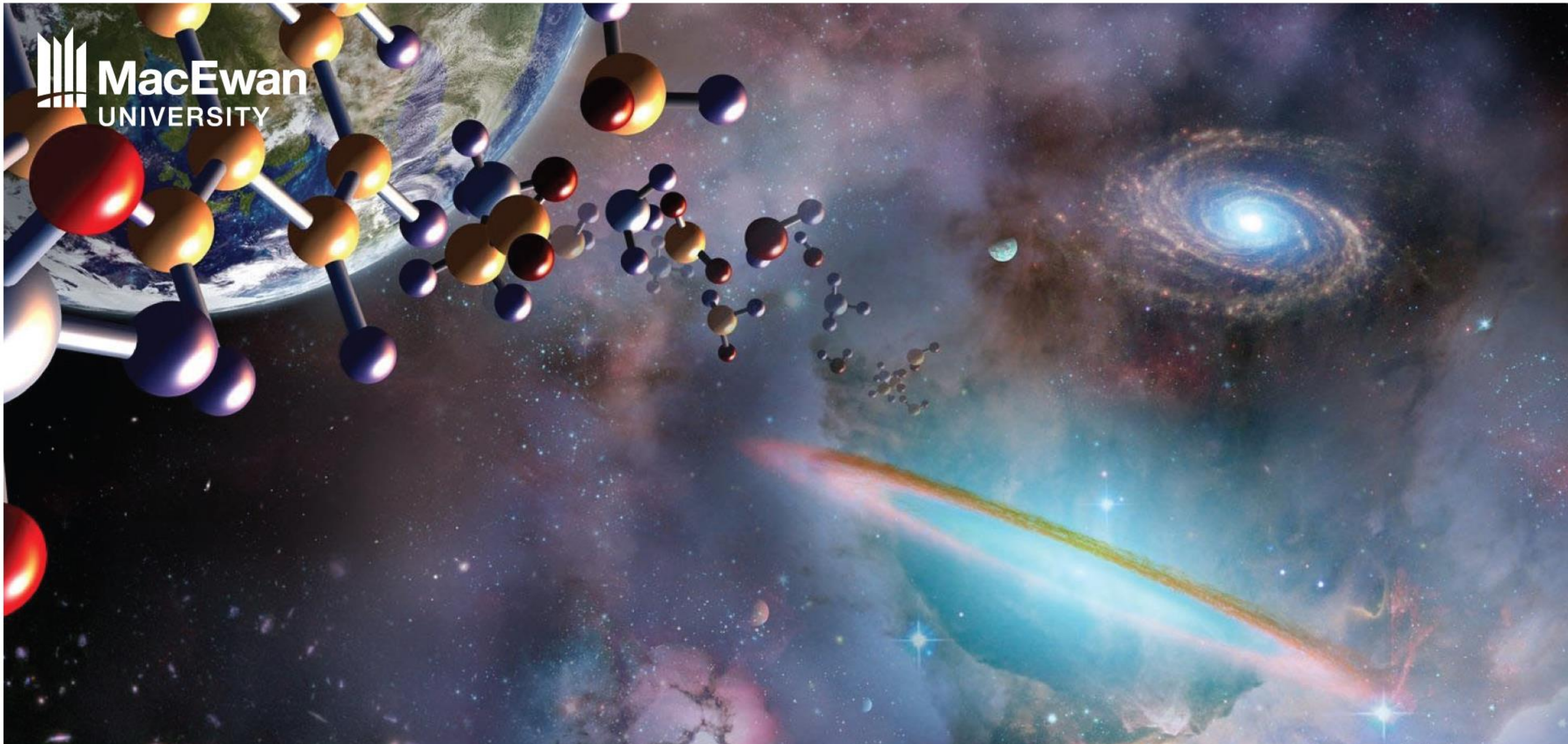

EXTRATERRESTRIAL ORGANIC COMPOUNDS IN OUR SOLAR SYSTEM:

Origins and Parent-Body Alterations

Tuesday, January 26, 2016

12:30 - 1:30 p.m.
Room 6-153, City Centre Campus

Presented by:
Dr. Robert Hilts, MacEwan University

Faculty of Arts and Science
DEPARTMENT OF PHYSICAL SCIENCES
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What is an organic compound?

The definition I will be using for this talk:

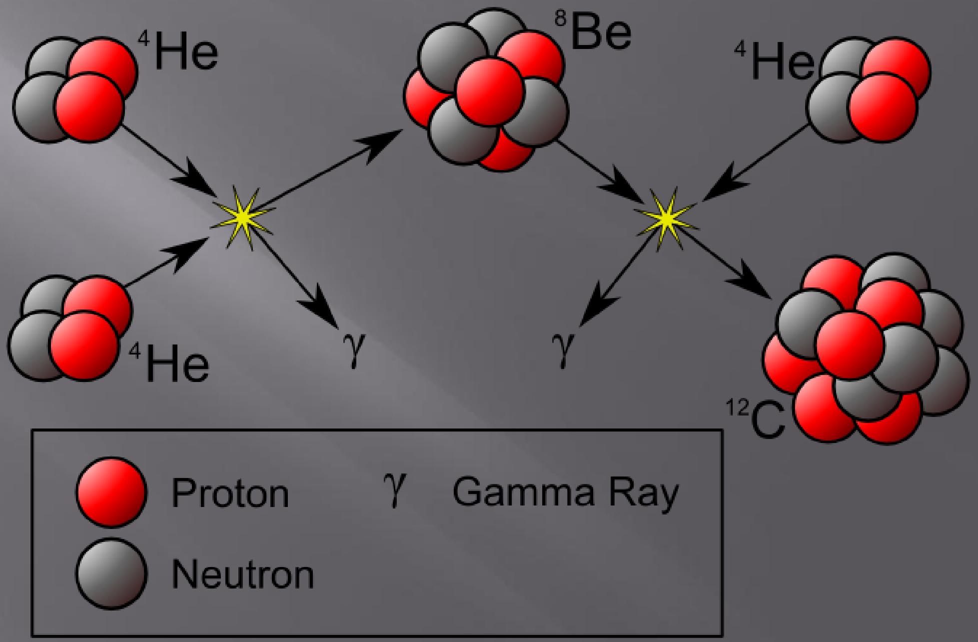
"For a species to be defined as an organic compound, it must possess at least one C-H bond"

e.g. HCCBr, LiCCH, CH_4, CH_3OH are organic compounds.

CaC_2, CO_2, H_2CO_3, $H_2C_2O_4$ are not organic compounds

The First-Generation Organic Compounds: Cold Chemistry in the Interstellar Medium

- All of the carbon in the universe is made by fusion reactions inside stars.
- Carbon-12 is created by the fusion of three helium-4 nuclei (triple alpha process)



- Carbon-13, nitrogen-14 and oxygen-16 are made late in the lives of red giant stars by CNO burning:

$$^{12}C + {}^{1}H \rightarrow {}^{13}N + \gamma$$

$$^{13}N \rightarrow \boxed{^{13}C} + e^{+} + \text{neutrino}$$

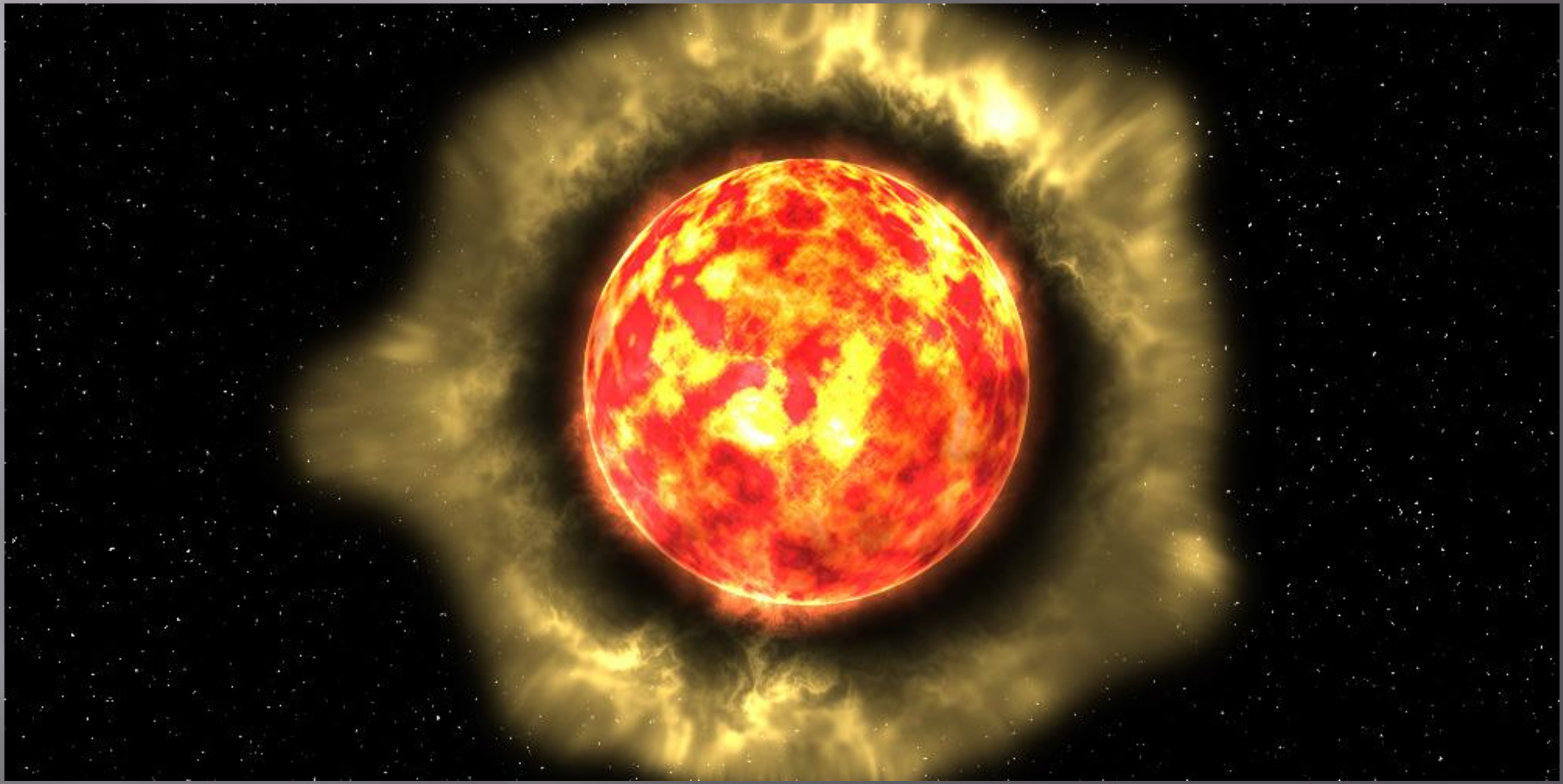
$$^{13}C + {}^{1}H \rightarrow \boxed{^{14}N} + \gamma$$

$$^{14}N + {}^{1}H \rightarrow {}^{15}O + \gamma$$

$$^{15}O \rightarrow {}^{15}N + e^{+} + \text{neutrino}$$

$$^{15}N + {}^{1}H \rightarrow \boxed{^{16}O} + \gamma$$

- Stars near the end of their lives expel C, N and O atoms into the interstellar medium during the shedding of their outer layers



- The ejected gas and dust eventually become *nebular clouds*.

Interstellar Organic Chemistry: Cold Nebular Syntheses of Simple Organic Molecules

- H and He together constitute ca. 70 % of the total mass of the interstellar medium (ISM).

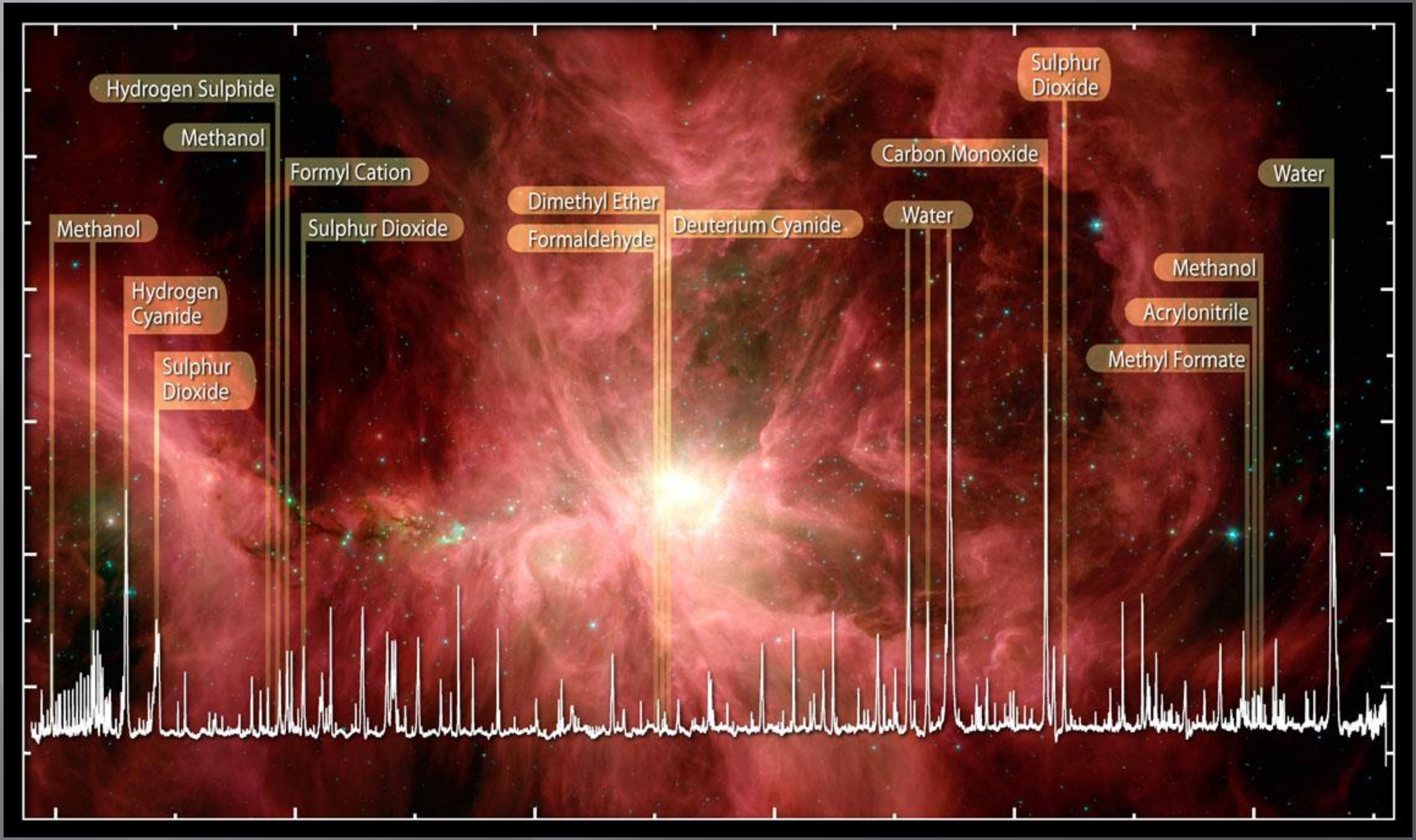
- The atoms C, O, N and S collectively account for ca. 1 % of the total mass in the ISM.

- About 1 % of the mass is in the form of micron-sized dust particles consisting of *graphite, PAHs, diamond, silicon, carbides, silicates* and *carbonates*

- Most of the dust in the ISM is collected in the nebular clouds.

- Numerous *organic compounds* have also been seen in nebulae.

- Organic compounds are, however, only a trace constituent of the ISM (less than 1 % of the total mass of the ISM is organics)



(Data from the Hershel Space Observatory)

Common Interstellar Organic Compounds (First-Generation Organic compounds)

H_3CNC

CH_4

H_3CCN

SiH_4

HCN

H_2CO

CH_3OH

$HCCH$

$HCOOH$

C_6H_6

$H_3C(O)H$

H_3CCOOH

- Interestingly, the inorganic compound *carbon monoxide* accounts for 20 % of the mass of carbon in the ISM.

- CO is formed by the free radical reaction of OH·, a species with a high abundance in the ISM, with atomic carbon:

$$OH^{\cdot} + C \rightarrow CO + H$$

- Because of its high abundance and great reactivity in the nebular cloud, CO is an important building block for many interstellar compounds.

Cold Nebular Reactions with Very Low Activation Energies

- The chemical reactions in interstellar clouds occur under rarified and extremely cold conditions.
- Under these conditions only reactions with negligible activation energies will proceed.
- Reactions between a positive ion and a neutral molecule or atom have negligible activation energies.
- It is likely that these positive ion - neutral molecule reactions are the ones responsible for the production of simple organics in nebular clouds.

- Positive ions are generated by electrons being knocked out of atoms or neutral molecules.

- Cosmic rays are the energy source for the production of positive ions in nebulae.

- Because the composition of these clouds is mostly H_2 and He, the first cations formed are He^+ and H_2^+.

- An important secondary process is the formation of the H_3^+ cation:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

- The trihydrogen monocation can combine with CO to form HCO^+, which is an important building block for oxygen-containing organic species:

$$H_3^+ + CO \rightarrow HCO^+ + H_2$$

- The secondary reaction of the helium cation with CO gives C^+:

$$He^+ + CO \rightarrow C^+ + He + O$$

- The C^+ cation is the basis for the rich organic chemistry in interstellar clouds:

(chain growth based on C^+)

$$C^+ + C_2H_4 \rightarrow C_2H_3^+ + H$$

$$C_2H_3^+ + C_2H_4 \rightarrow C_4H_6^+ + H$$

etc.

- Here are a few more important interstellar synthetic organic reactions that occur in nebulae:

$$CH_3^+ + H_2O \rightarrow CH_3OH_2^+$$

$$CH_3OH_2^+ + e^- \rightarrow CH_3OH + H$$

$$C^+ + OH_2 \rightarrow HCO^+ + H$$

$$HCO^+ + H_2 \rightarrow H_2CO + H^+$$

$$CO_2 + H_3^+ \rightarrow HCOOH + H^+$$

$$N^+ + H_2 \rightarrow NH_2^+$$

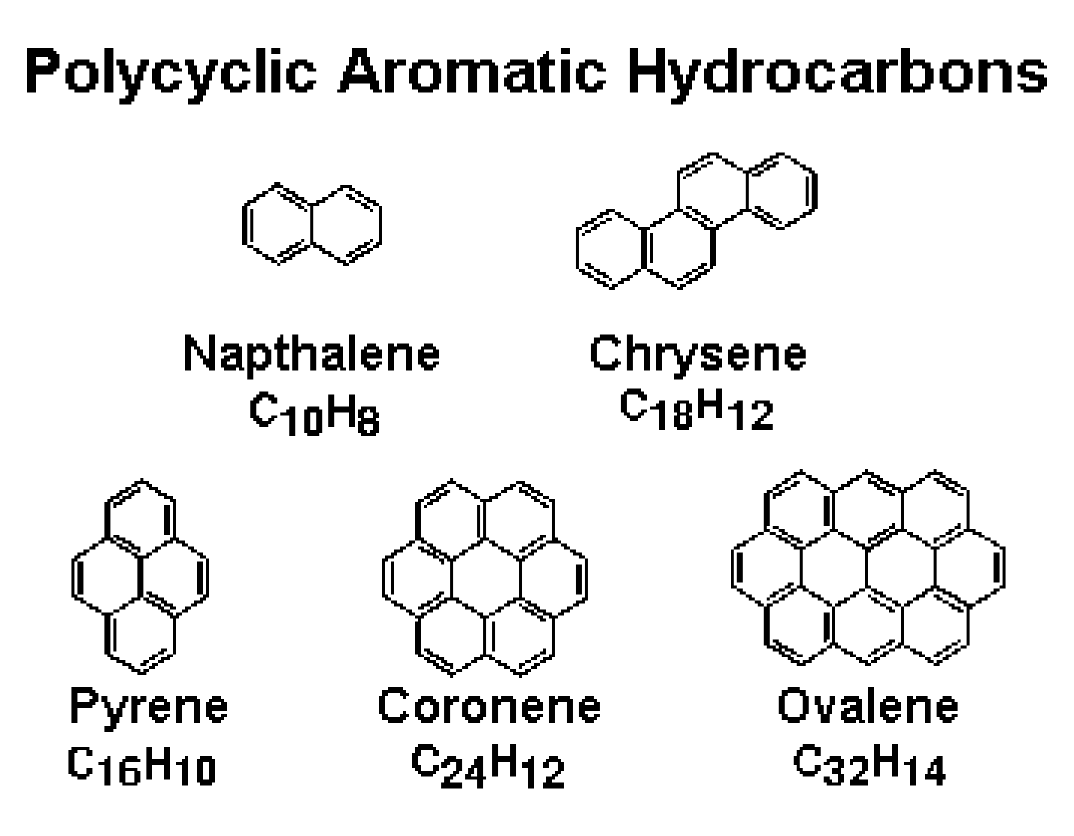
$$NH_2^+ + H_2 \rightarrow NH_3 + H^+$$

$$C^+ + N \rightarrow CN^+$$

$$CN^+ + H_2 \rightarrow HCN + H^+$$

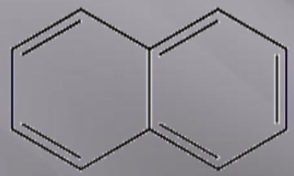
Interstellar Synthesis of More Complex Organics: Low Temperature Assembly of PAHs

- PAHs (polycyclic aromatic hydrocarbons), which are organic molecules composed of fused benzene rings, are key molecules in the astrochemical evolution of the interstellar medium.



- PAHs are believed to provide critical nucleation sites for the formation of carbonaceous dust particles.

- The discovery of napthalene (the simplest PAH) in 20 carbonaceous chondrites suggests an interstellar origin



$C_{10}H_8$

- Recently it has been proposed that napthalene, the prototypical PAH, in formed in nebulae via a free radical reaction between the phenyl radical and vinyl acetylene:

$$3\,HC \equiv CH \quad + h\nu \rightarrow \quad C_6H_6$$

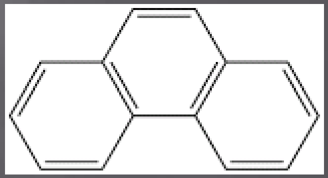
$$C_6H_6 \quad + h\nu \rightarrow \quad H^{\cdot} \quad + \quad C_6H_5^{\cdot}$$

$$C_6H_5^{\cdot} \quad + \quad CH_2 = CH - C \equiv CH \quad \rightarrow \quad C_{10}H_8 \; + \; H^{\cdot}$$

- Higher molecular weight PAHs rings are formed through the addition of vinylacetylene to PAH radicals that have additional fused rings.

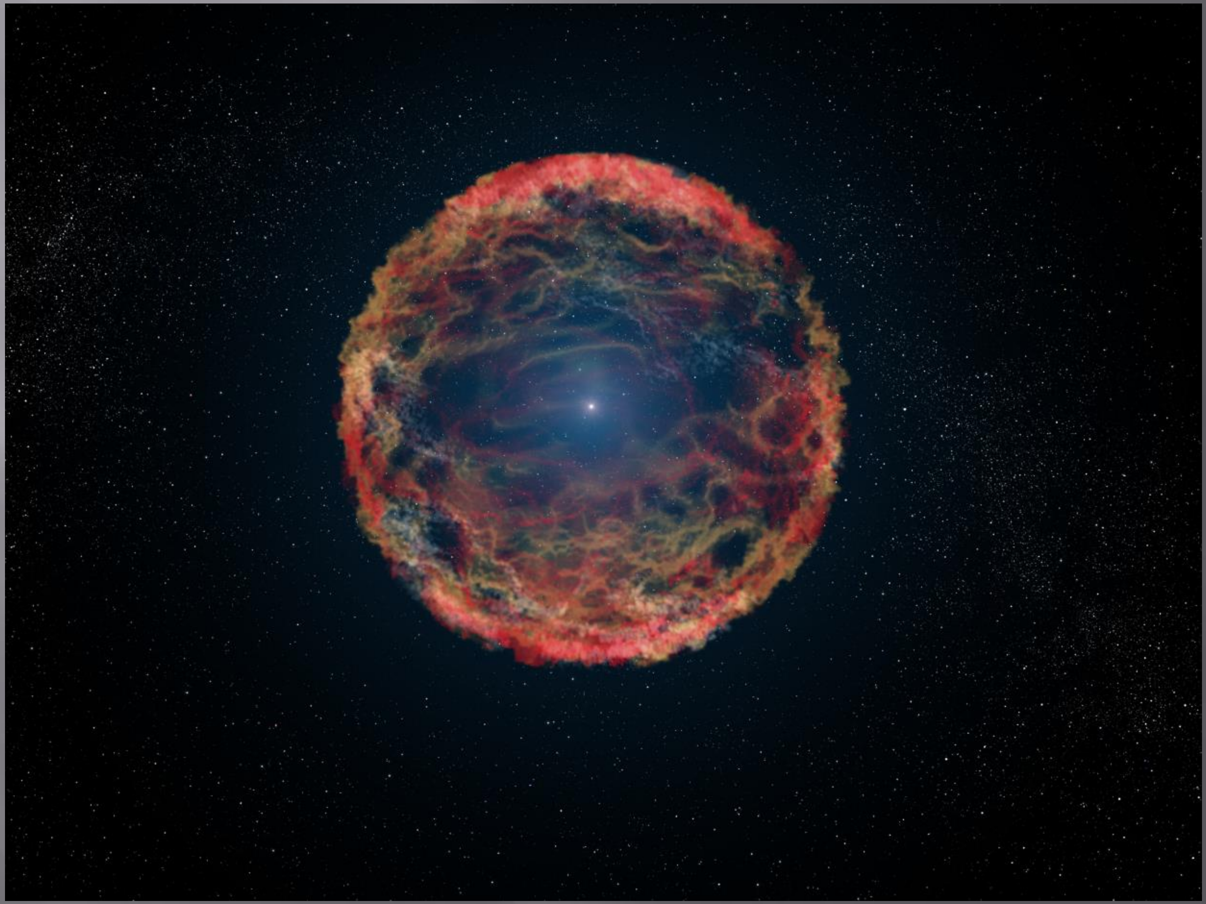
e.g. The napthyl radical reacts with vinylacetylene to form phenanthrene:

$$C_{10}H_7^{\cdot} \quad + \quad CH_2 = CH - C \equiv CH \rightarrow C_{14}H_{10} \; + \; H^{\cdot}$$



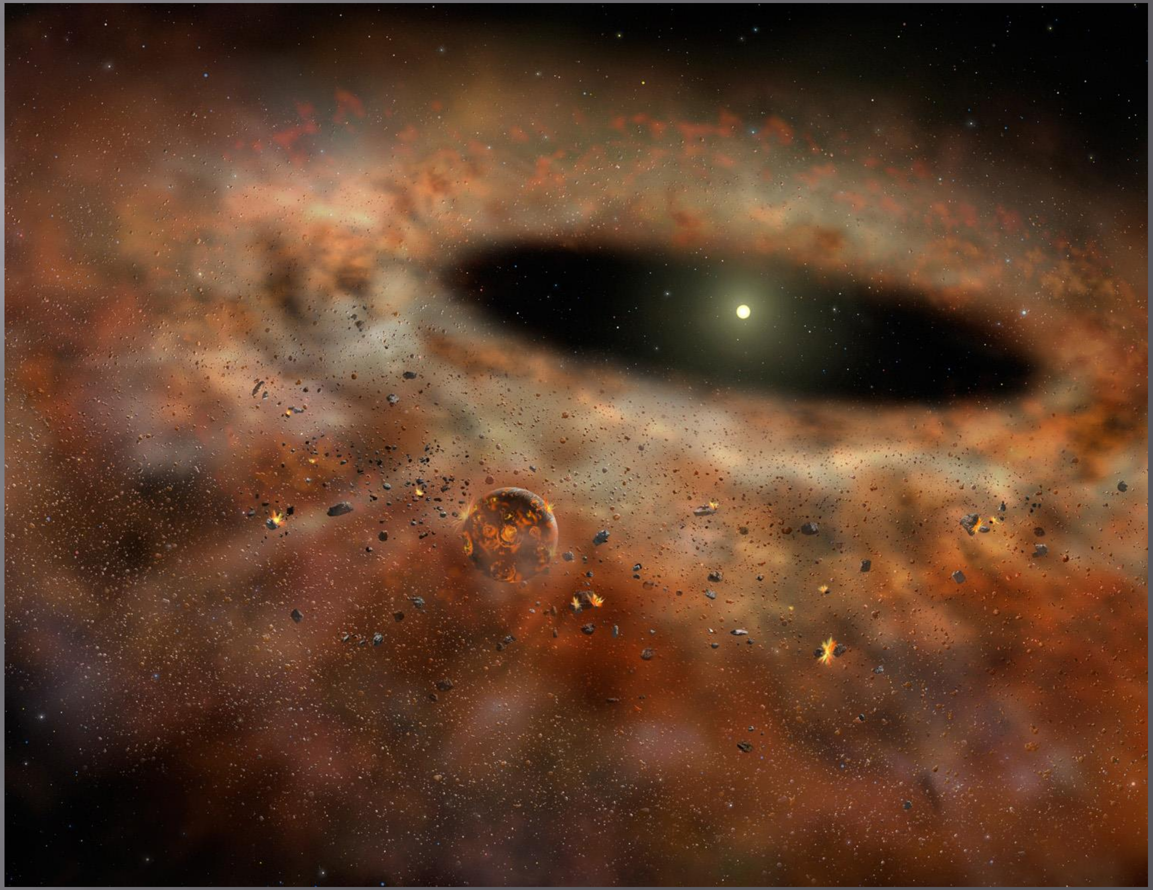
Migration of the First Generation Organics into the Protoplanetary Disk

- Ca. 4.6 billion years ago the shock wave from an exploding star helped to trigger the formation of our solar system.

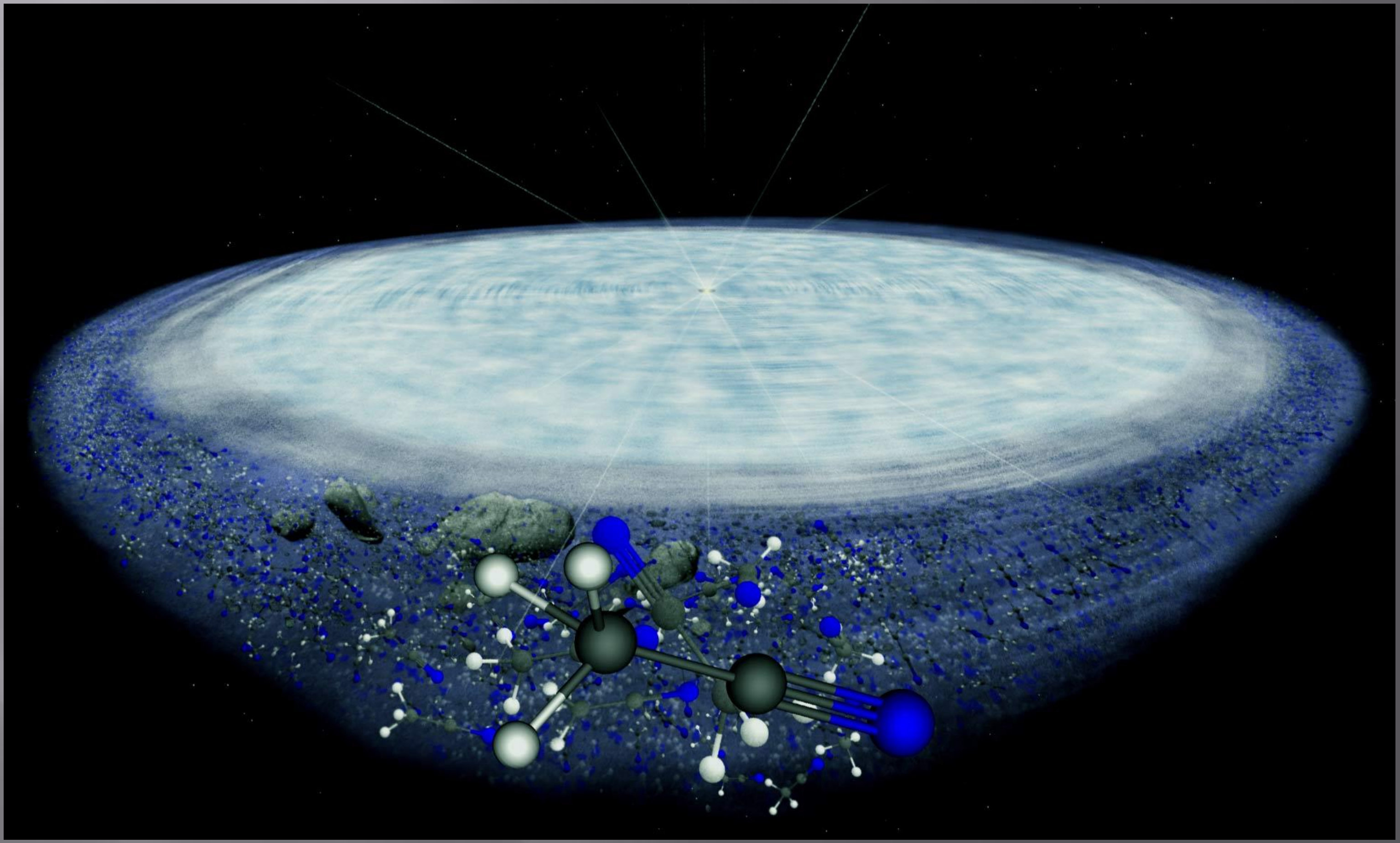


- The shock wave compressed the nebula causing it to collapse into a spinning cloud of dust and gas called the solar nebula

- The original inventory of simple, first-generation organics became part of the solar disk.



- The organics ended up adsorbed on the surface of ice grains or trapped within small asteroidal bodies composed of chondritic material.



- The shock wave injected material form the exploding star into our solar nebula

- The evidence of this pollution by exogenous stellar material comes from the contents of primitive chondrites, which were the first solid materials to condense form the solar nebula.

- Meteoriticists found the decay elements of short-lived radionuclides in the CAIs (calcium-rich aluminum inclusions) of ancient chondrites, which formed ca. 4.57 billion years ago).

(e.g. the decay products of Fe-60, which can only be formed in supernova explosions were found in several chondrite stones)

- The organics captured in the nebula were subjected to high temperatures and a high flux of UV radiation by the new star.

- This lead to significant secondary processing of most of the first generation organics into more complex second-generation organics.

- Thus, evolution of the organic matter proceeded during planetary formation.

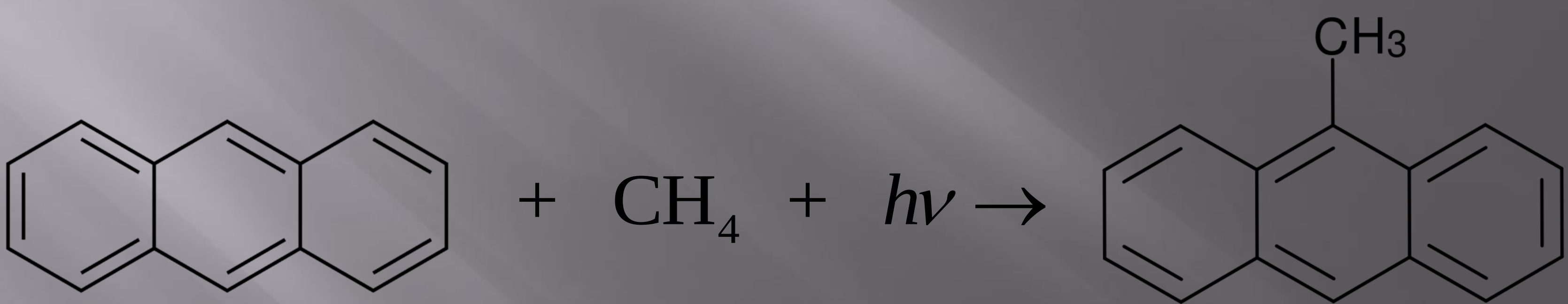
- The decay of radioactive nuclei within the undifferentiated planetesimals generated enough heat to produce liquid water, which altered both the minerals and the organics within the parent bodies.

- Ultimately, small sections of the parent bodies were blasted off by collisions with other bodies and the fragments fell into the inner solar system.

- As soon as the fragments enter the earth's atmosphere they are reclassified as *meteorites* (derived form the Latin word *meteorum,* which means any atmospheric phenomenon)

Second-Generation Organic Compounds formed in our solar system or in the ISM: Photochemical transformations on icy dust grains and the surfaces of primitive parent bodies

Alkylation of Polycyclic Aromatic Hydrocarbons



Methyl-radical driven alkyl chain elongation reactions

$$CH_4 + h\nu \rightarrow CH_3^{\cdot} + H^{\cdot}$$

$$CH_3^{\cdot} + HCOOH \rightarrow CH_4 + COOH^{\cdot}$$

$$COOH^{\cdot} + CH_3^{\cdot} \rightarrow CH_3COOH$$

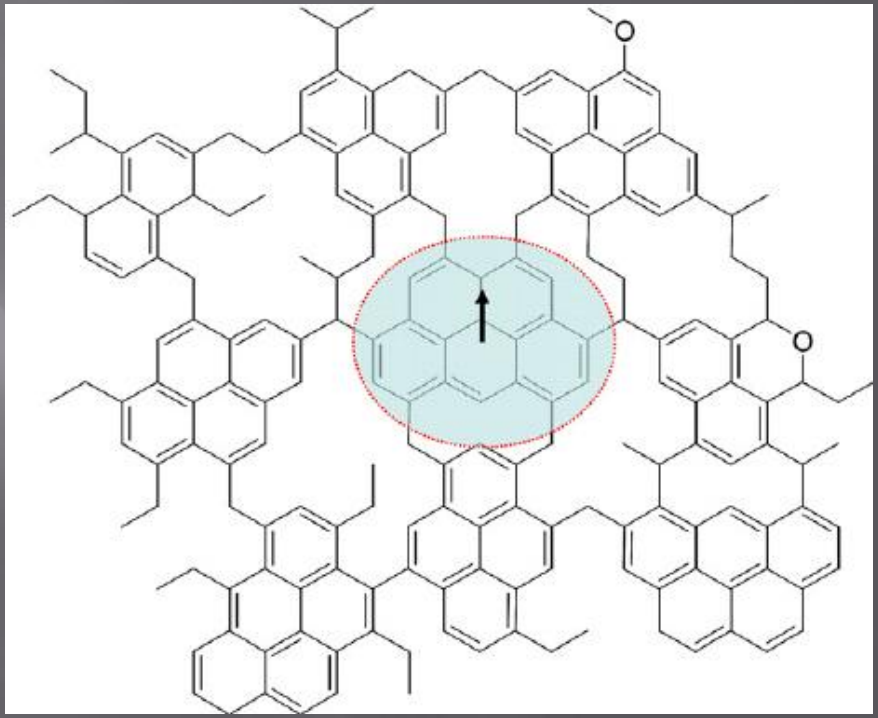
$$CH_3^{\cdot} + CH_3COOH \rightarrow CH_4 + CH_2COOH^{\cdot}$$

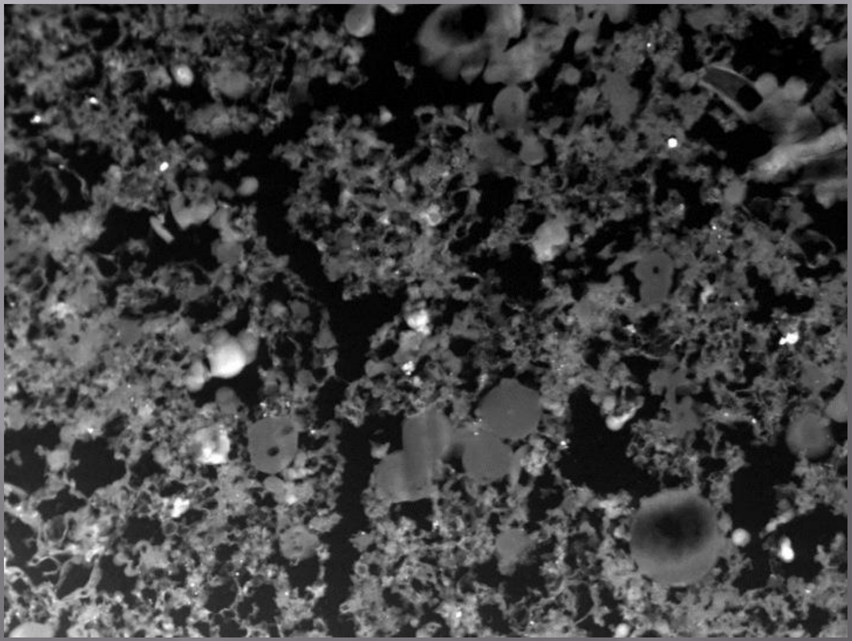
$$CH_2COOH^{\cdot} + CH_3^{\cdot} \rightarrow CH_3CH_2COOH$$

etc.

Formation of insoluble organic matter (macromolecular species composed of PAH islands joined by bridging alkyl groups)

Alkylated PAHs + $h\nu \rightarrow$

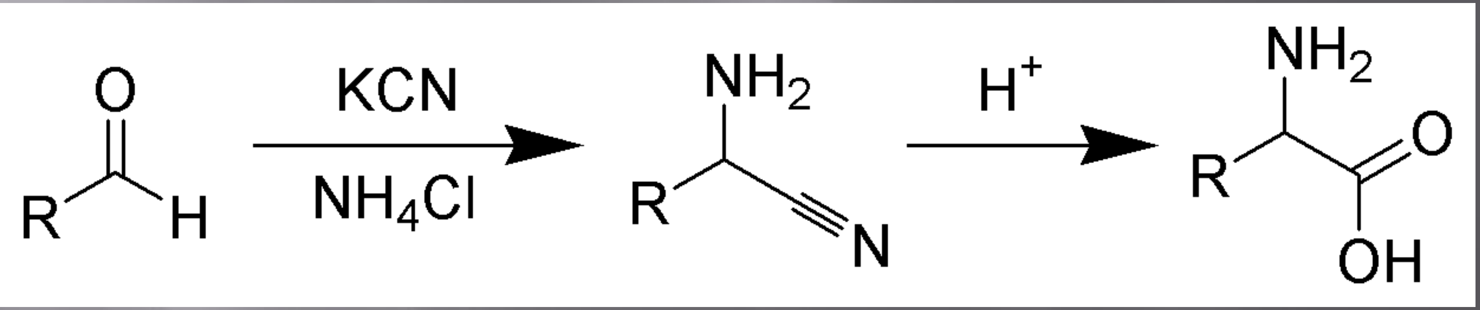




IOM in a carbonaceous chondrite

Second-Generation Organic Compounds formed in our solar system or in the ISM: Hydrothermally-Driven organic transformations on icy dust grains and within primitive parent bodies

The Strecker synthesis of amino acids

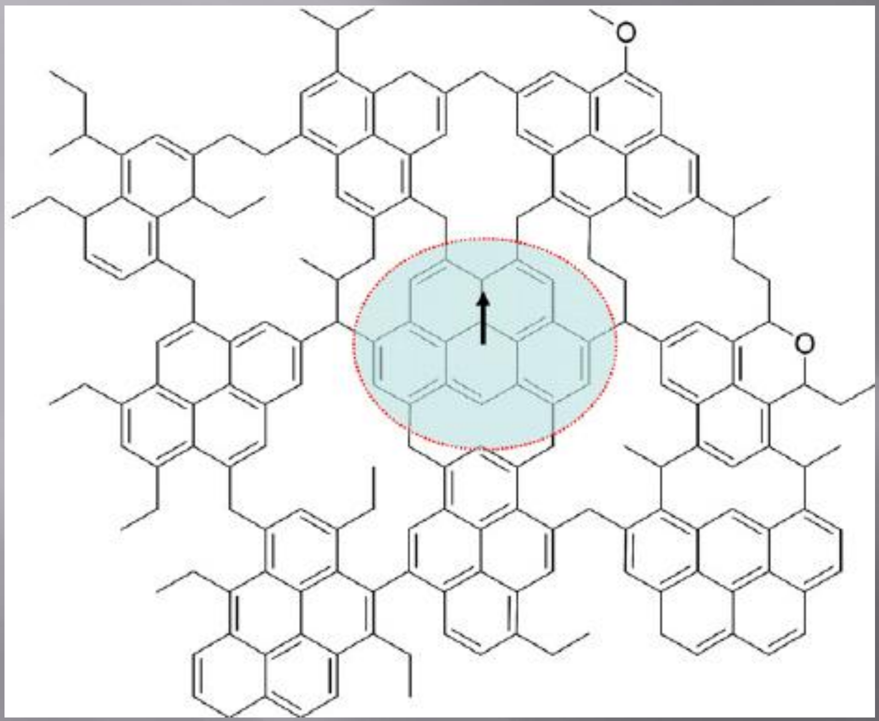


Formation of carboxylic acids by oxidation of aldehydes or alcohols

$$HC(O)H + \text{mineral oxidant} \rightarrow HCOOH$$

$$CH_3OH + \text{mineral oxidant} \rightarrow CH_3COOH$$

Hydrothermal degradation of IOM



+ heat/H_2O →

carboxylic acids + alkyl phenols + kerogen

Chemical Modification of Interstellar Organics on the Moon and Planets

Tholins : The first macromolecular CN material

- Tholins (Greek word for mud) are complex mixtures of unsaturated macromolecular species containing C,H and N.
- Tholins are produced by irradiating gaseous mixtures of methane and dinitrogen gas.
- Thus, the tholin reaction coverts interstellar methane and dinitrogen into a reddish-brown organic polymer.

- Tholins are typically found on planetary surfaces that lie beneath atmospheres containing dinitrogen and methane.
- They also form at the interface between icy surfaces of moon and underlying oceans that contain dissolved organics.
- Tholins were probably formed on the primordial Earth (before the advent of oxygen, the Earth's atmosphere contained substantial quantities of CH_4 and dinitrogen)

- An artist's impression of how the Earth looked ca. 3.5 billion years ago; aerosol tholins dominate the sky

Primary Photodissociation Reactions in Titan's atmosphere

$$CH_4 + h\nu \rightarrow CH_2 + H_2$$

$$CH_4 + h\nu \rightarrow CH + H_2 + H$$

$$CH_4 + h\nu \rightarrow C + 2H_2$$

(< 160 nm)

$$N_2 + h\nu \text{ (or } e^-) \rightarrow N + N$$

(< 80 nm)

Titan's Atmosphere: Primary Formation Reactions

NC + CC → NCCC

NCCC + CN → NCCCCN

CN + CN → NCCN

N + CH_2 → HCN + H

N + H_2CN → $H_2C{=}N{=}N$

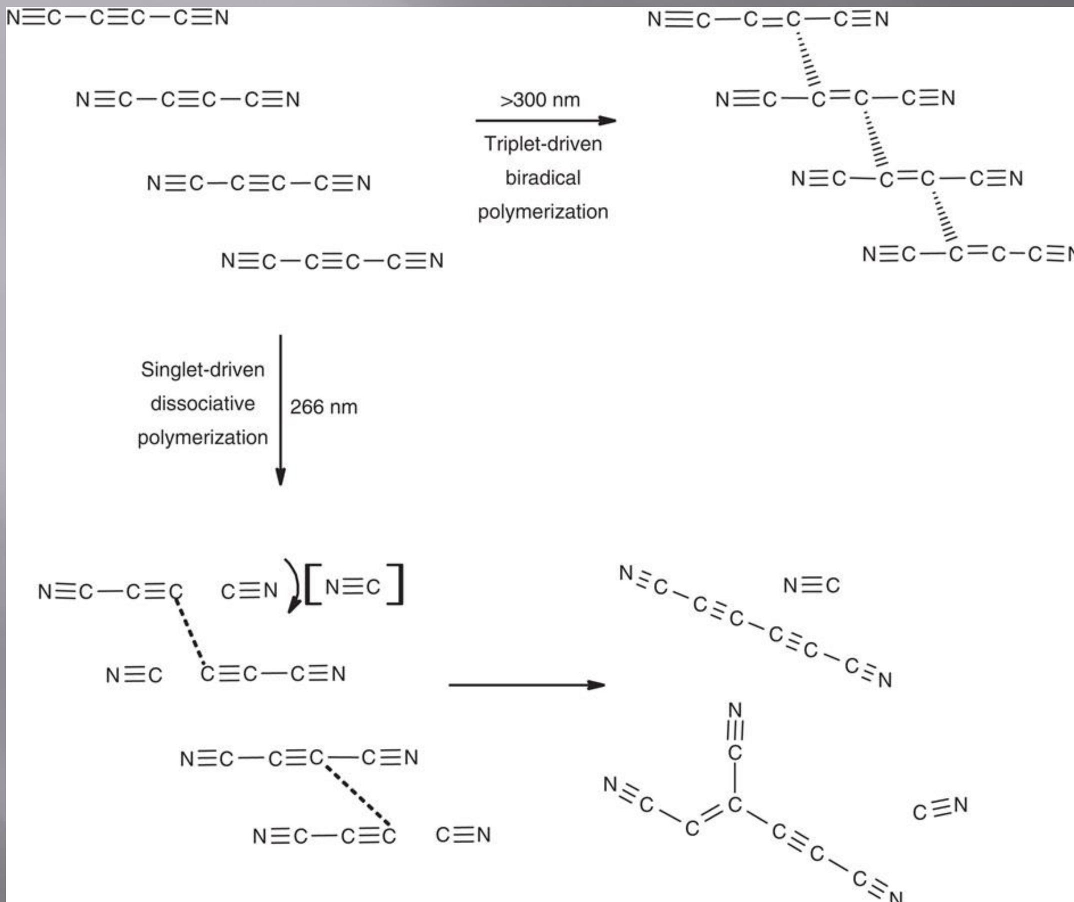
N + CH_3 → HCN + H_2

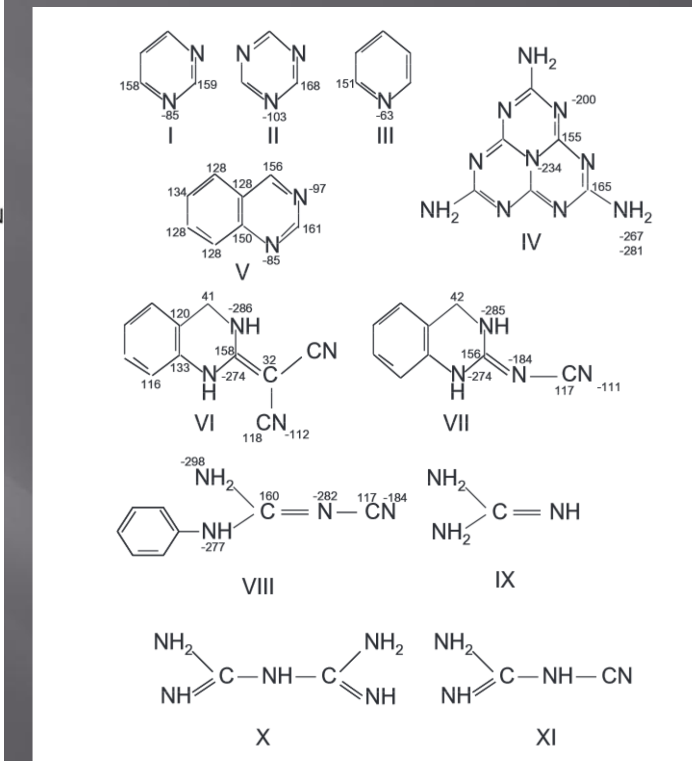
NH_2 + CH_3 → H_2NCH_3

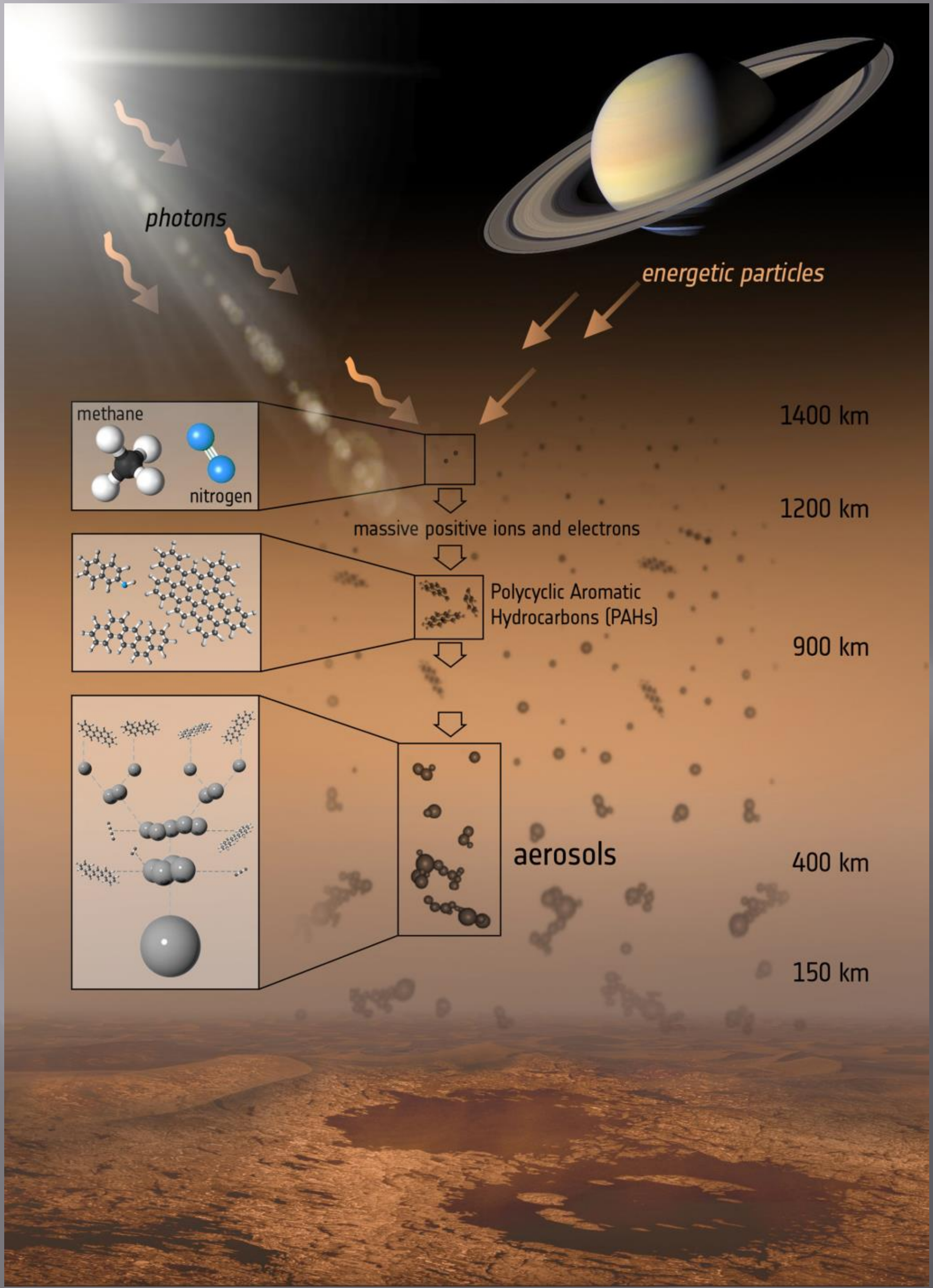
2 NH_2 + CH_2 → $H_2NCH_2NH_2$

CH_2 + RNC → $H_2C{=}C{=}NR$

Gas-phase synthesis of tholins

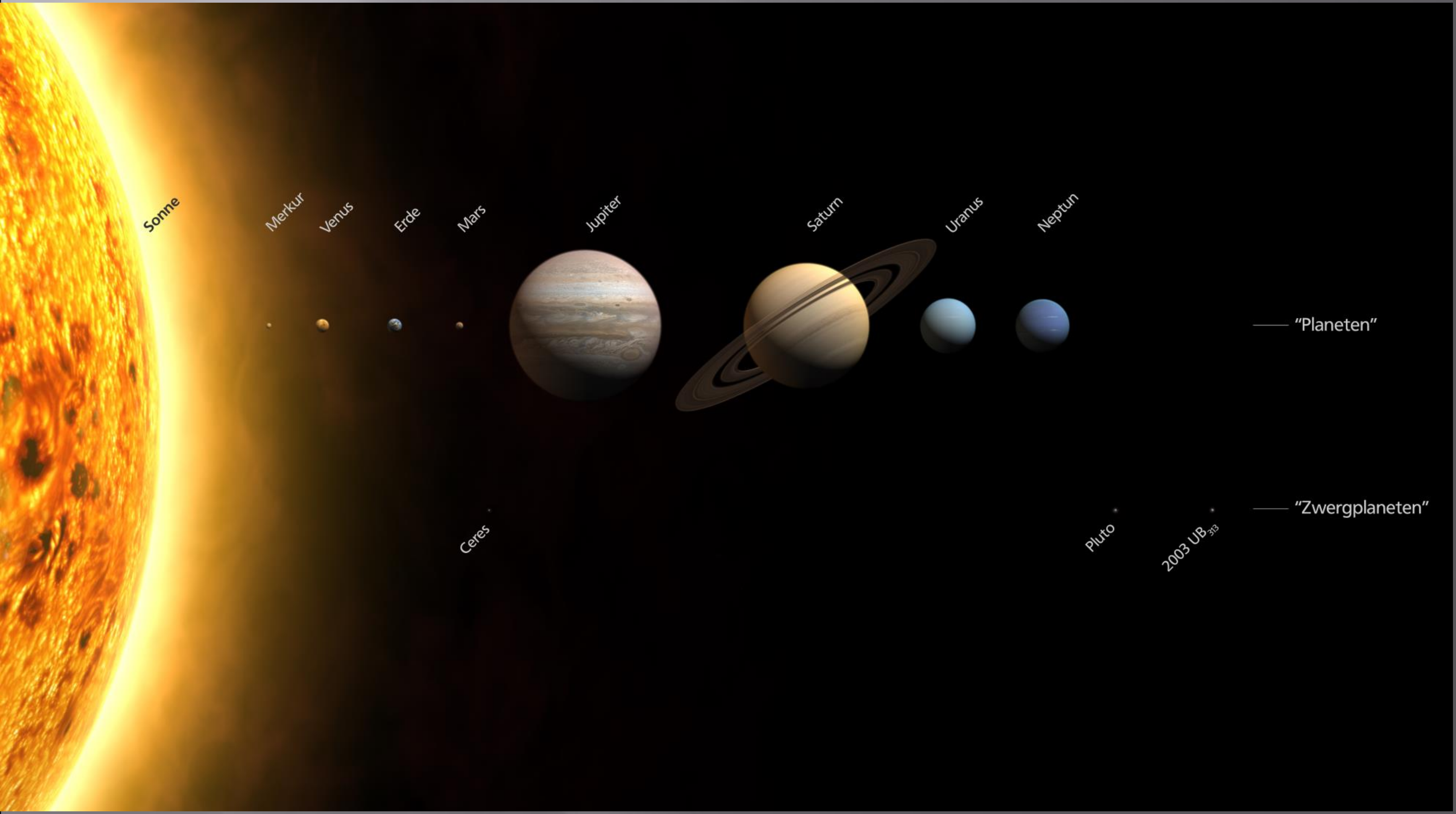






Tholins on Titan:
A Complex mixture of polynitriles, PAHs and polycyanides that rain down on the surface

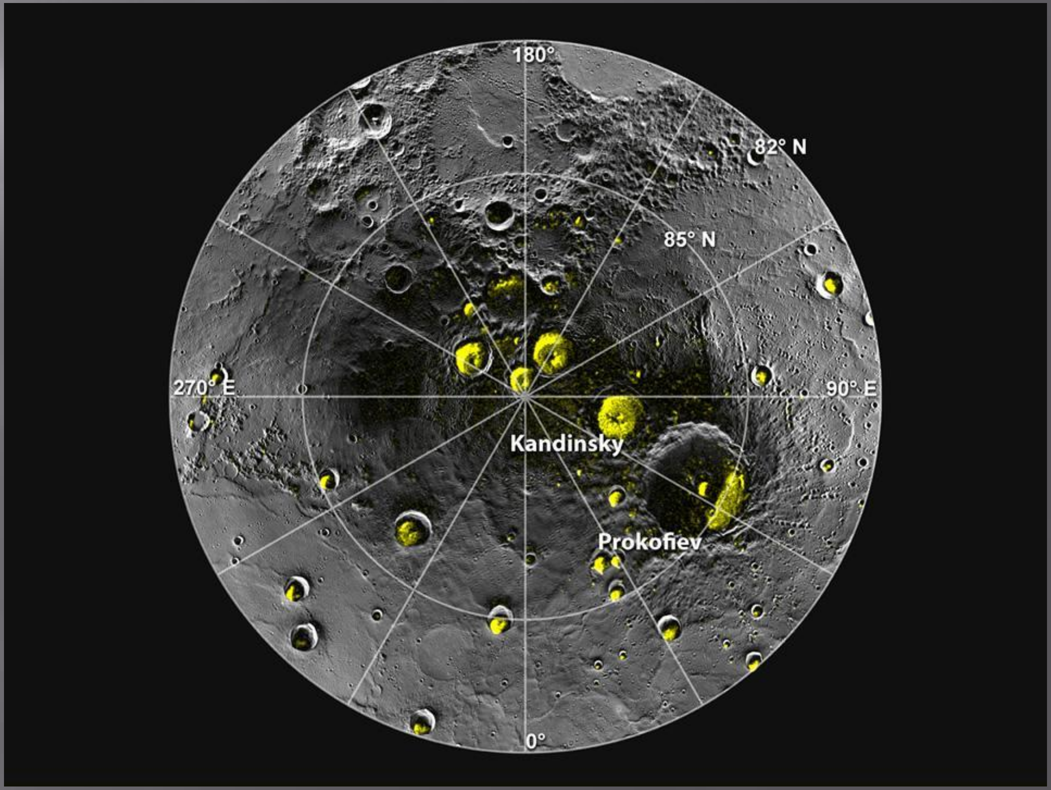
What is the Solar System's organic budget?
Where the extraterrestrial organics located?



The Extraterrestrial Organics in Our Solar System: an almost complete survey

Mercury

- The MESSENGER spacecraft found abundant water ice and first-generation interstellar organics in permanently shadowed polar craters on Mercury

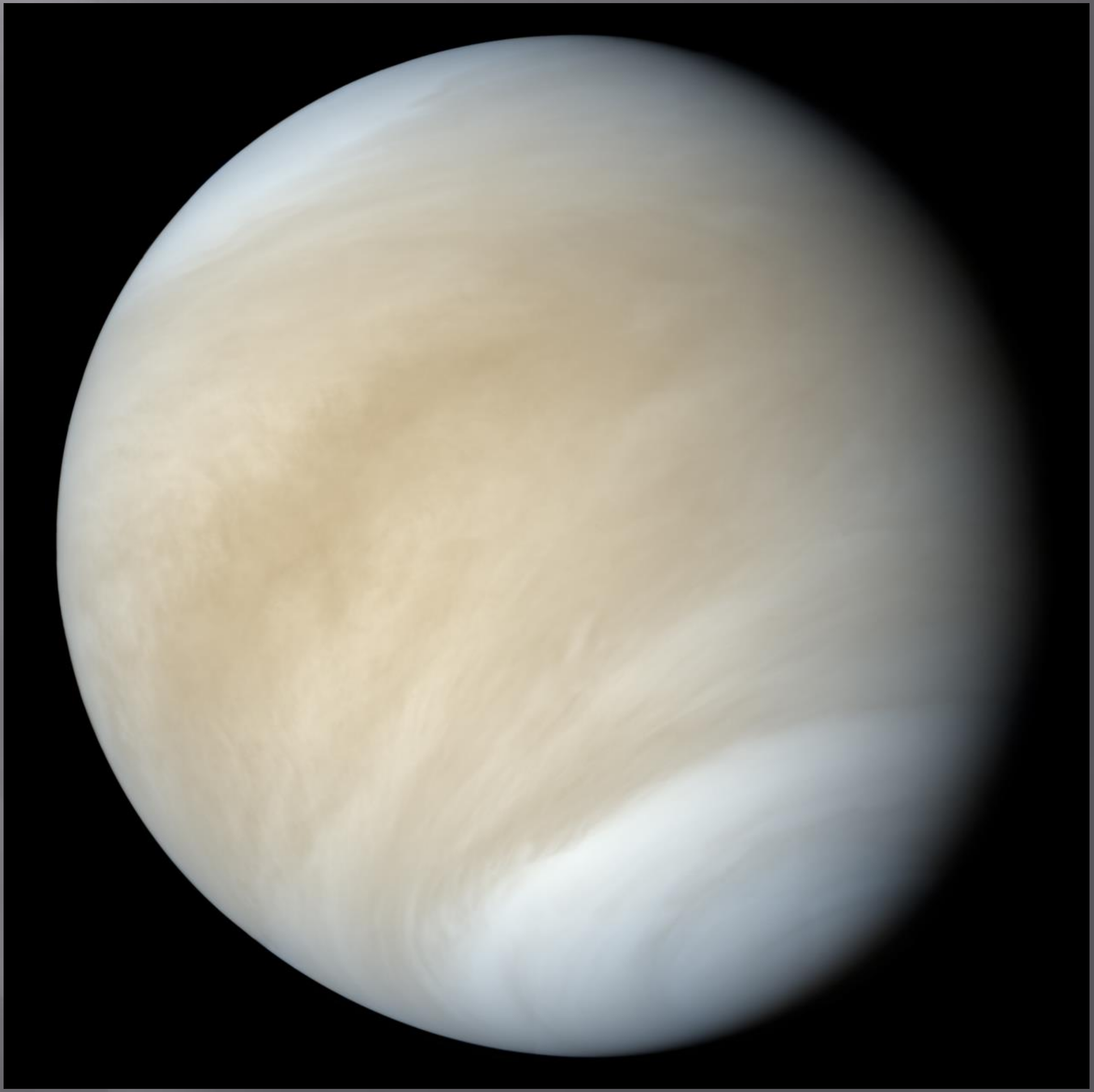


Venus

- We are virtually certain that there are no organic compounds on the surface or in the rocks of Venus

- Not surprisingly, no organics have been detected in the atmosphere as well

(460ºC on Venus, 90 atm pressure of CO_2)



- Mixing of any organics on the surface of Venus with oxidizing magma would result in the total conversion of all organic species into carbon dioxide and water (water would be lost via photodegradation reactions)

e.g.

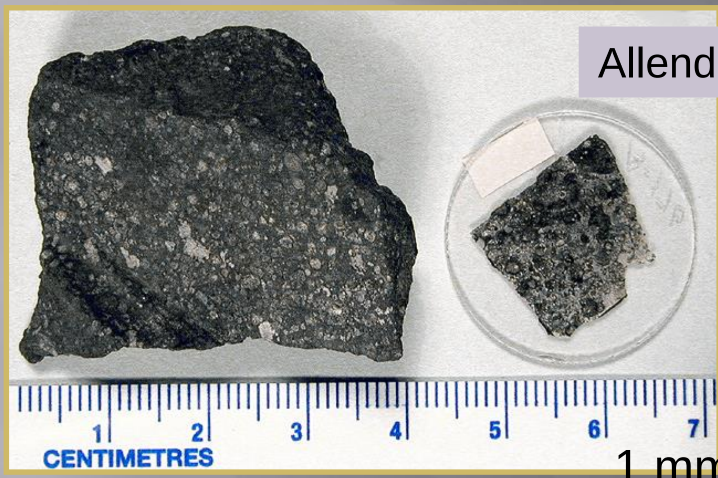
$$C_6H_6 + \text{heat} \rightarrow C(s) + 3H_2(g)$$

$$2FeO(\text{in basalt}) + C(s) \rightarrow CO_2 + 2Fe$$

Earth

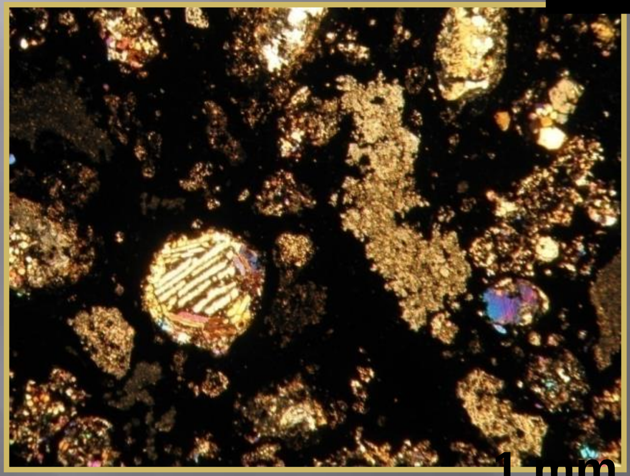
- The only place where extraterrestrial organic compounds can be found on the earth is inside carbonaceous chondrites and Martian meteorites!

Carbonaceous Chondrites

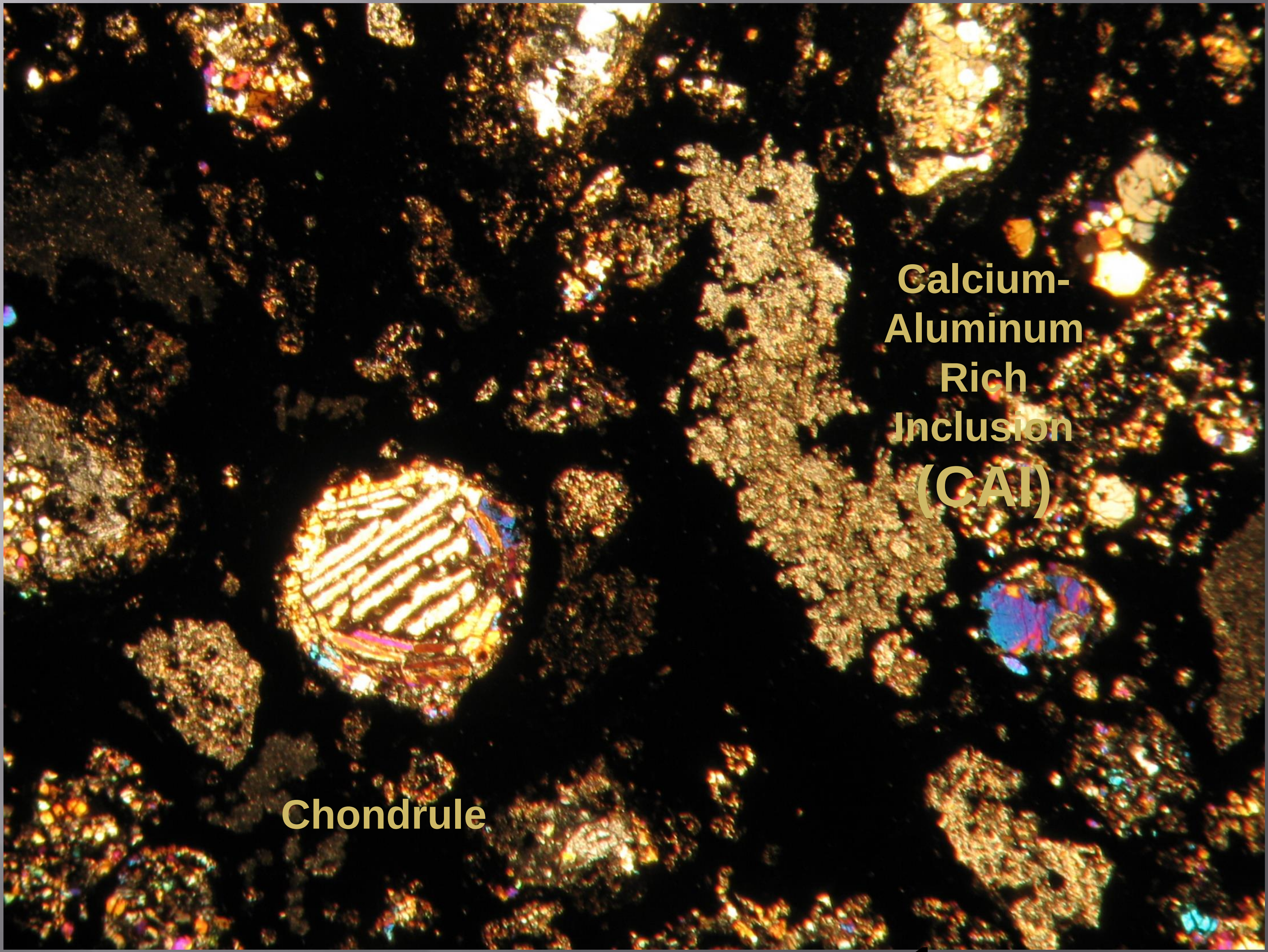


Allende

1 mm


1 mm

- Very primitive meteorites that have escaped heating/melting and planet formation (stayed undifferentiated)
- Information they provide:
  - Processes in the early Solar System
  - Types of nearby stars



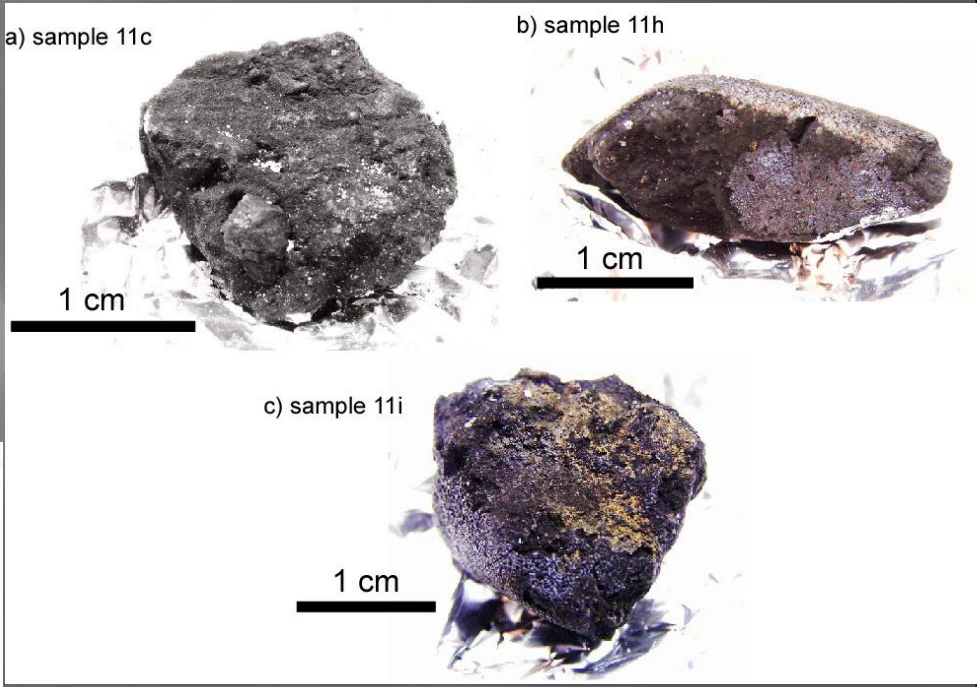
1 mm

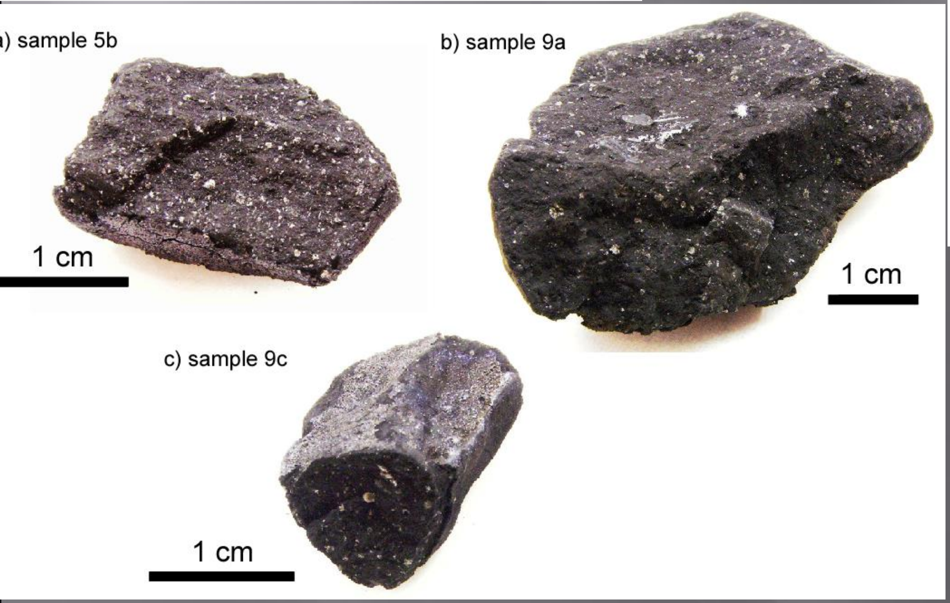
The Tagish Lake Meteorite

Image of Sample 2 courtesy of Ian Nicklin, Royal Ontario Museum

- Ungrouped carbonaceous chondrite
- Most C-rich chondrite (Grady et al. 2002)
  - 5.8 wt% total C
  - 2.6 wt% organic C
  - 2% of organic C is soluble
- Organic species in TL have been studied by only a few groups

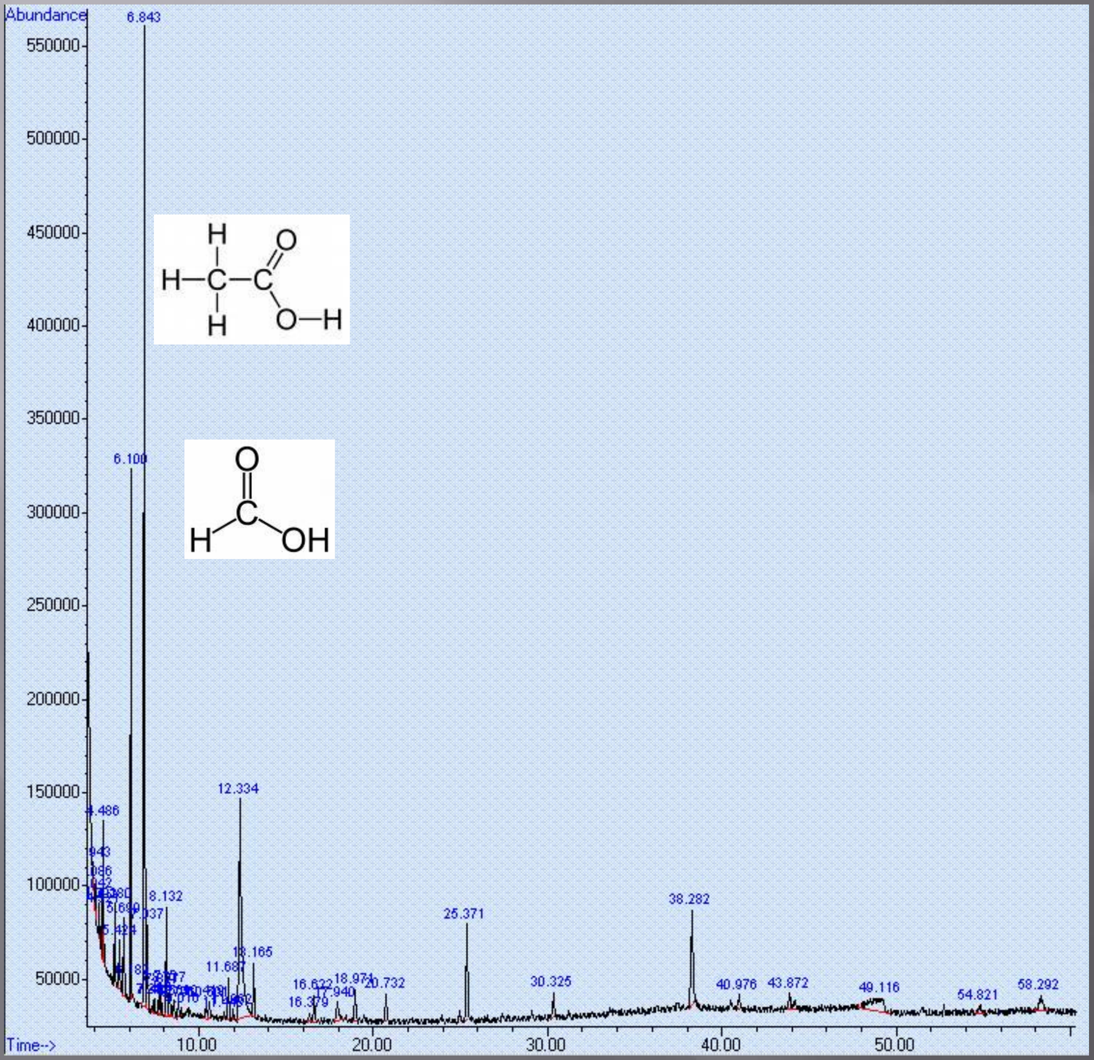
Pristine Material





Four lithologies studied: 11v(dust), 11i, 11h and 5b

GC Trace of the Water Extract of 11v



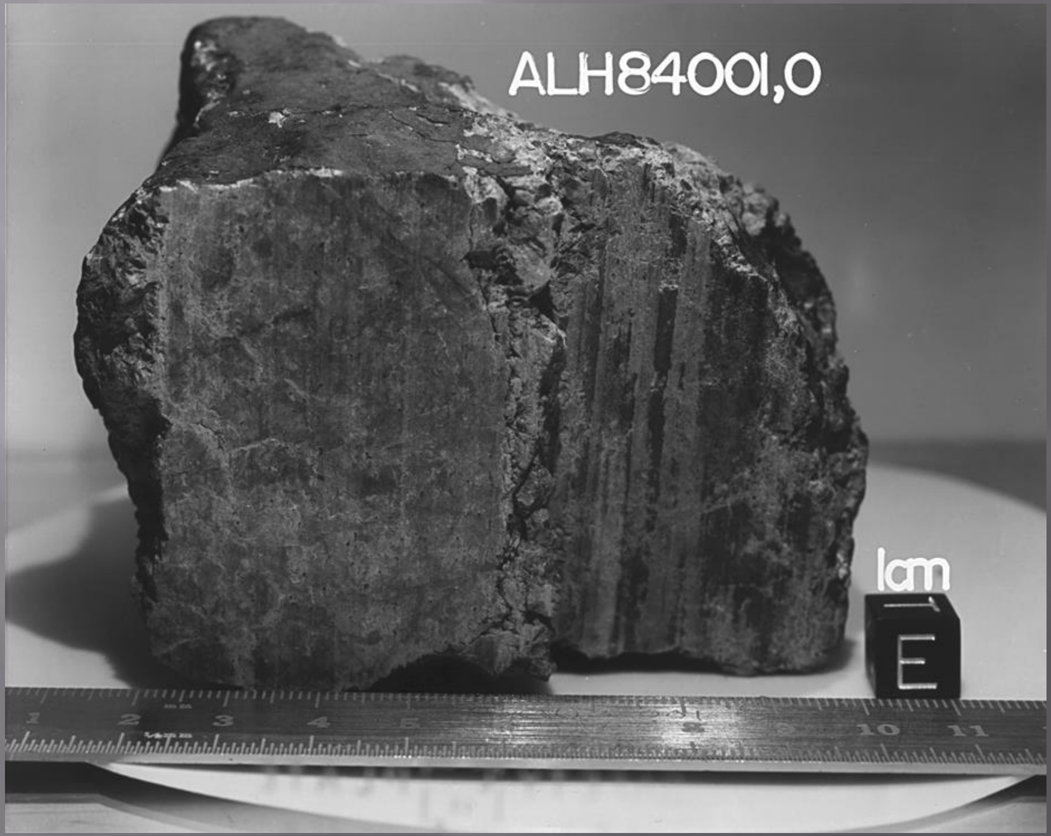
- Majority of the signals correspond to linear monocarboxylic acids(derived from alkanes)
- Most of C_1-C_{10} homologous series is present
- Formic acid is the predominant monocarboxylic acid (unprecedented)
- Formic acid-acetic acid ratio is 3:1

Formic Acid Abundances in Carbonaceous Chondrites

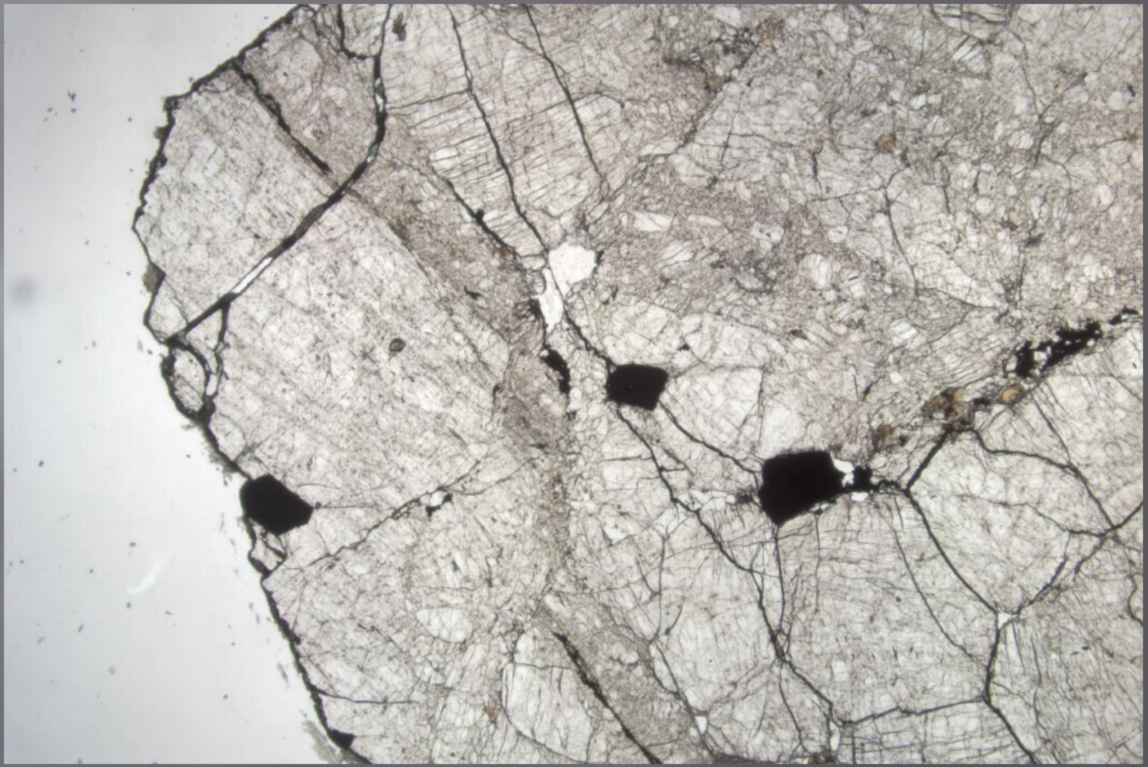
Meteorite	Detection Method	Concentration (ppm)	Reference
Tagish Lake (11i)	GC-MSD	200	LPSC 2009
Tagish Lake (11v)	GC-MSD	120	LPSC 2009
Murchison	GC-FID	2	Huang et al 2005
EET96029.20	GC-FID	50	Huang et al 2005
GRA 95229	GC-MS	< 1	Pizzarello et al 2008

Martian Meteorites

- The most famous Martian meteorite, ALH84001 was collected from the Allan Hills blue ice sheet in 1993

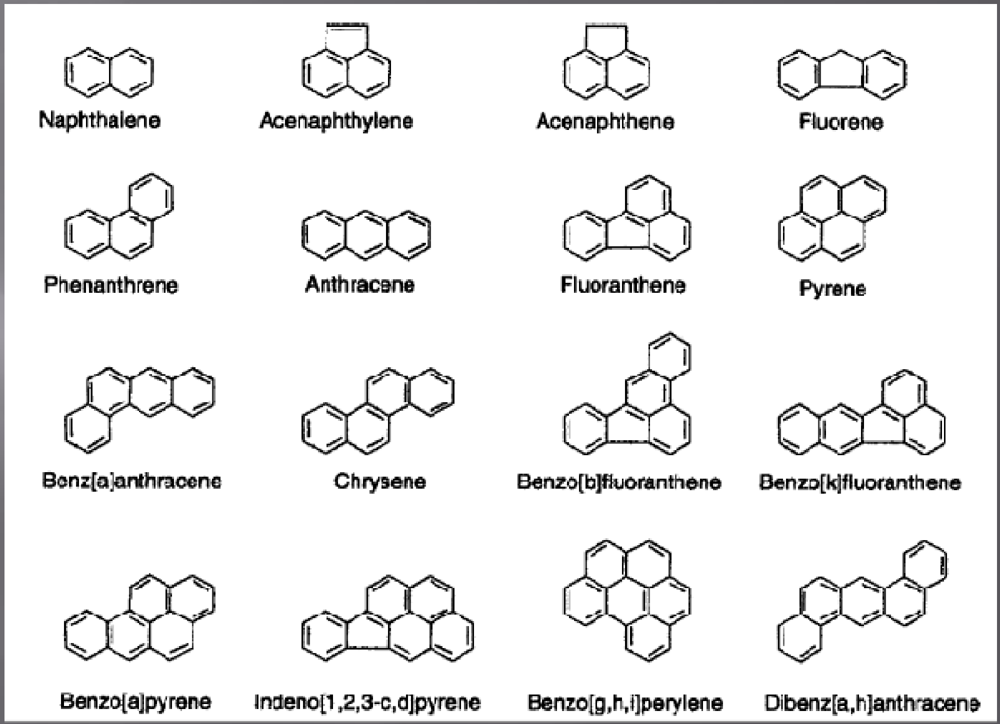


- PAHs were found inside carbonate globules within the interior of the meteorite.
- First observation of an organic compound in a Martian meteorite.

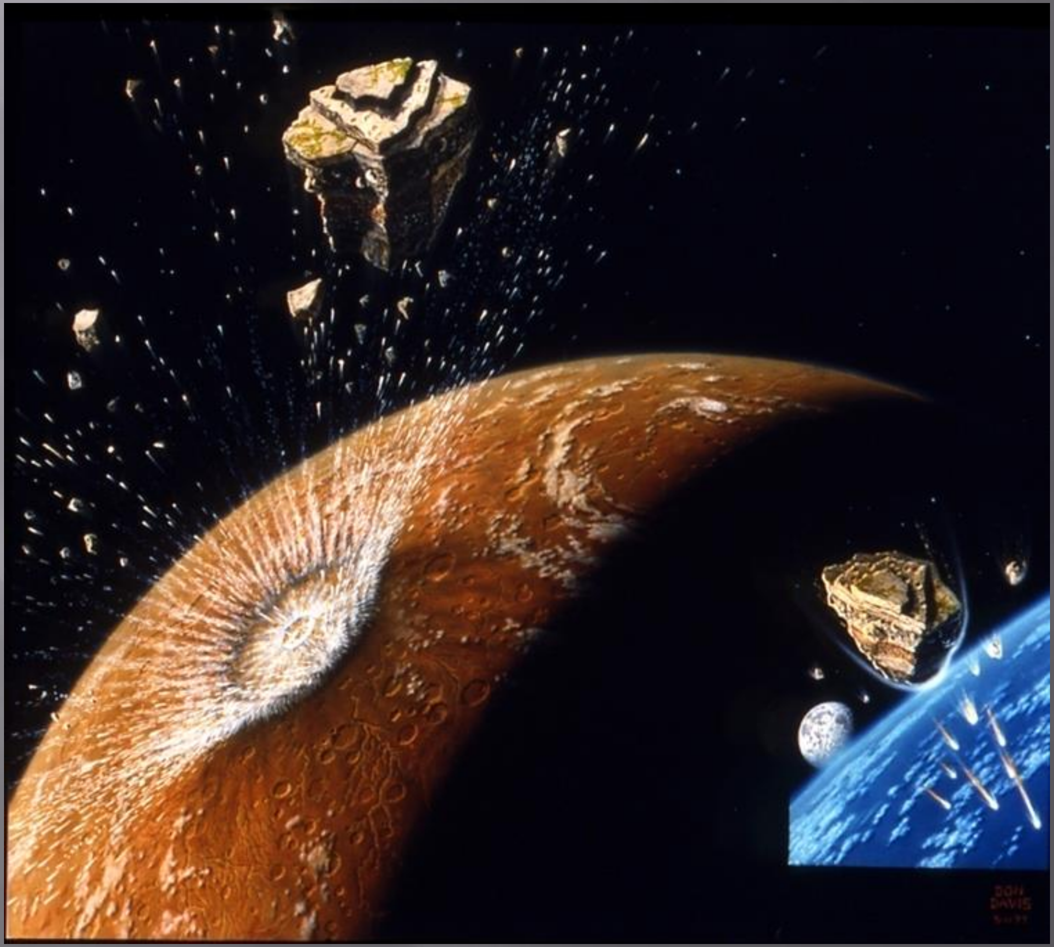


(Thin section of AL84001)

- The PAHs are likely ancient, first-generation molecules from the interstellar medium that were delivered to Mars by meteorites or comets billions of years ago.

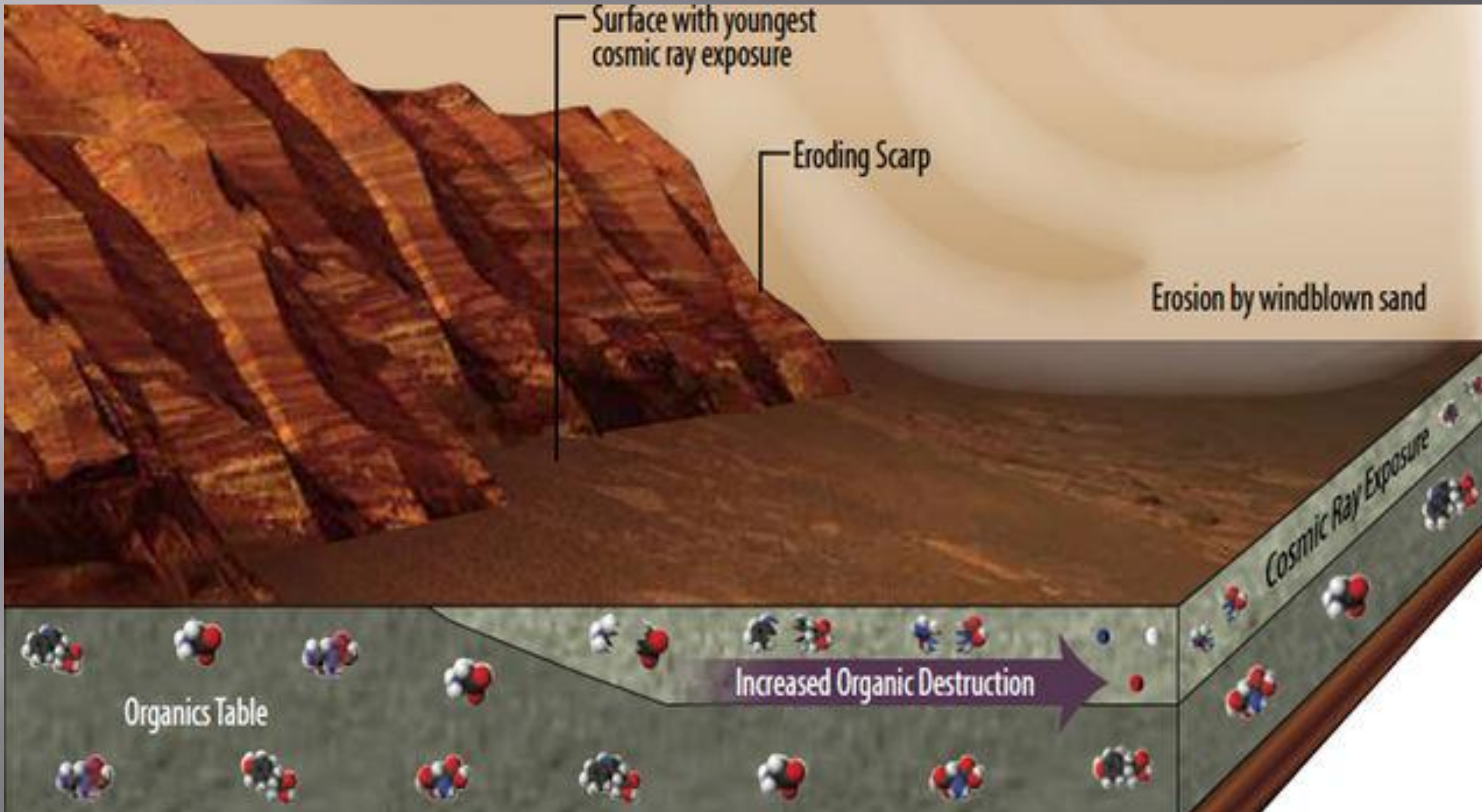


- Martian meteorites are believed to have been ejected from deep in the Martian crust by bolide impacts (bolide: a large meteorite)



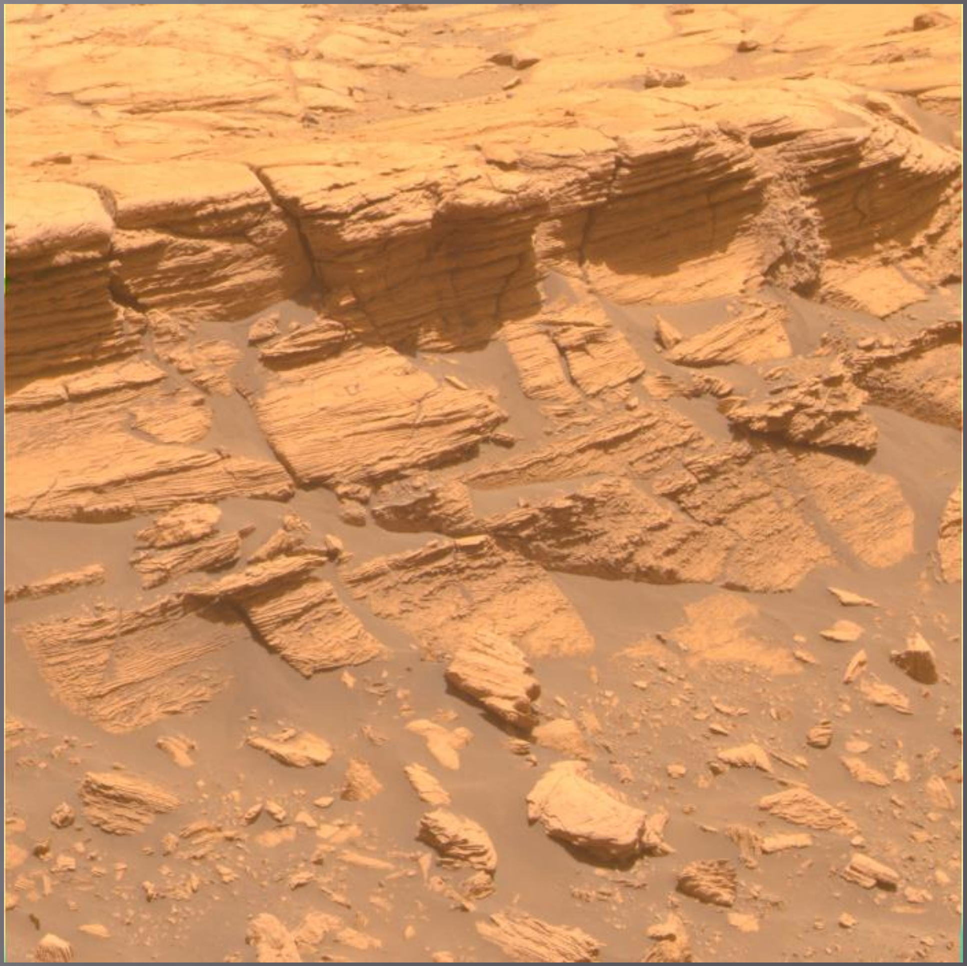
Mars

- No reduced organic species have been detected on the surface of Mars.
- Presently on the surface of Mars, the high UV/cosmic ray flux combined with the presence of hydrogen peroxide and perchlorate salts in the soil (both are good oxidizing agents), guarantees that any deposited or exposed organics will be quickly oxidized to CO_2 and water.
- However, any organics that were delivered to Mars in the distant past (when Mars had a thicker atmosphere) and then buried under at least a meter of soil should have survived.


Surface with youngest
cosmic ray exposure
Eroding Scarp
Erosion by windblown sand
Cosmic Ray Exposure
Increased Organic Destruction
Organics Table

- Amino acids and their amine degradation products have been found in an ancient *jarosite* sample on the Earth (jarosite is an evaporitic sulfate mineral Formula: $K(Fe^{3+})_3(OH)_6(SO_4)_2$

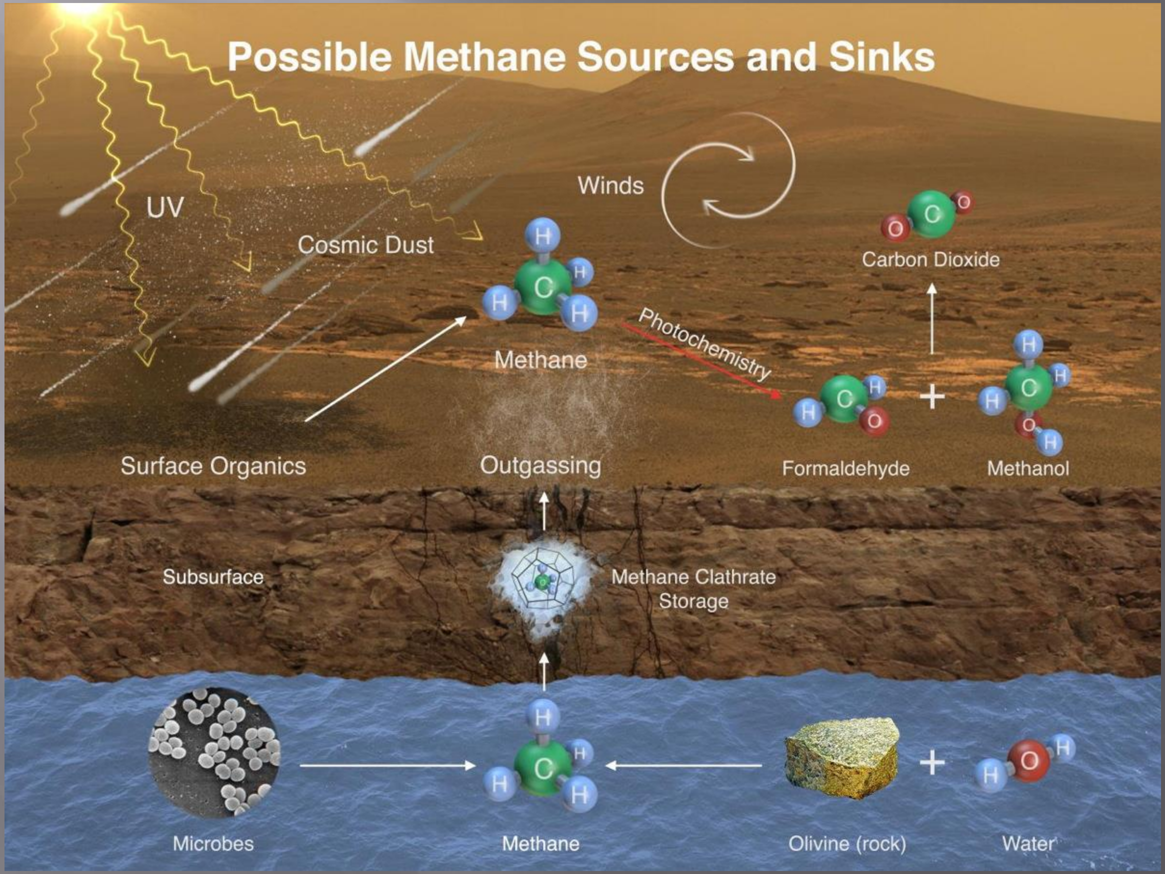
- Thus, the sulfate formations on the shores and sea beds of ancient oceans should be the prime targets in the search for organic compounds on Mars.



(Jarosite in Meridiani Planum)

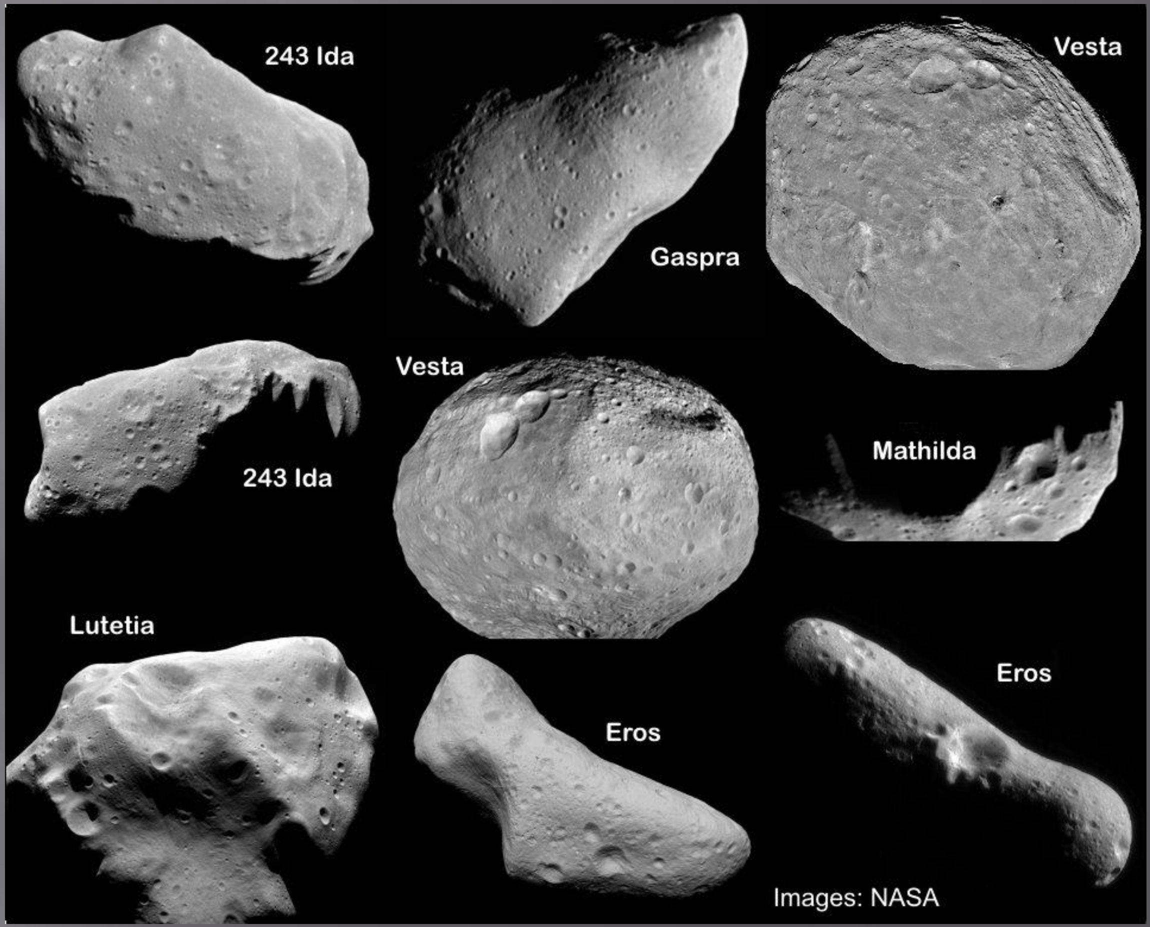
- What is likely first-generation interstellar methane has been detected in the atmosphere of Mars by the Curiosity rover.

- Methane has a short lifetime in the atmosphere: it is quickly photolyzed to carbon dioxide and water.



The Asteroid Belt

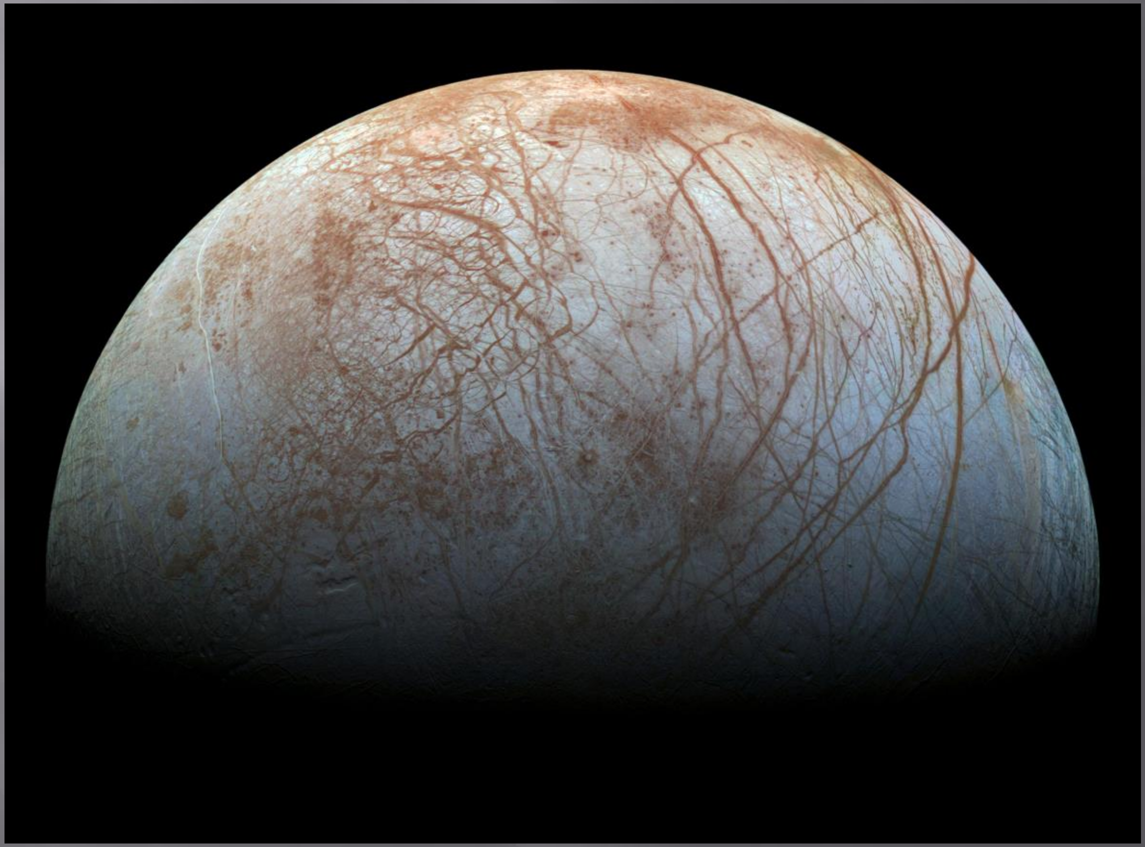
- The parent bodies for most meteorites are located in the asteroid belt.
- There no surface organics on asteroiods: the lack of an atmosphere precludes the formation of tholins and any surface organics would be destroyed by the solar UV radiation and cosmic rays



The Jovian System: Europa

- The only moon of Jupiter that exhibits clear evidence of the presence of surface organics is Europa.

- Red coloured regions on Europa may be tholin-like macromolecular solid material that is produced when surface ices containing organic compounds are exposed to incident energy.

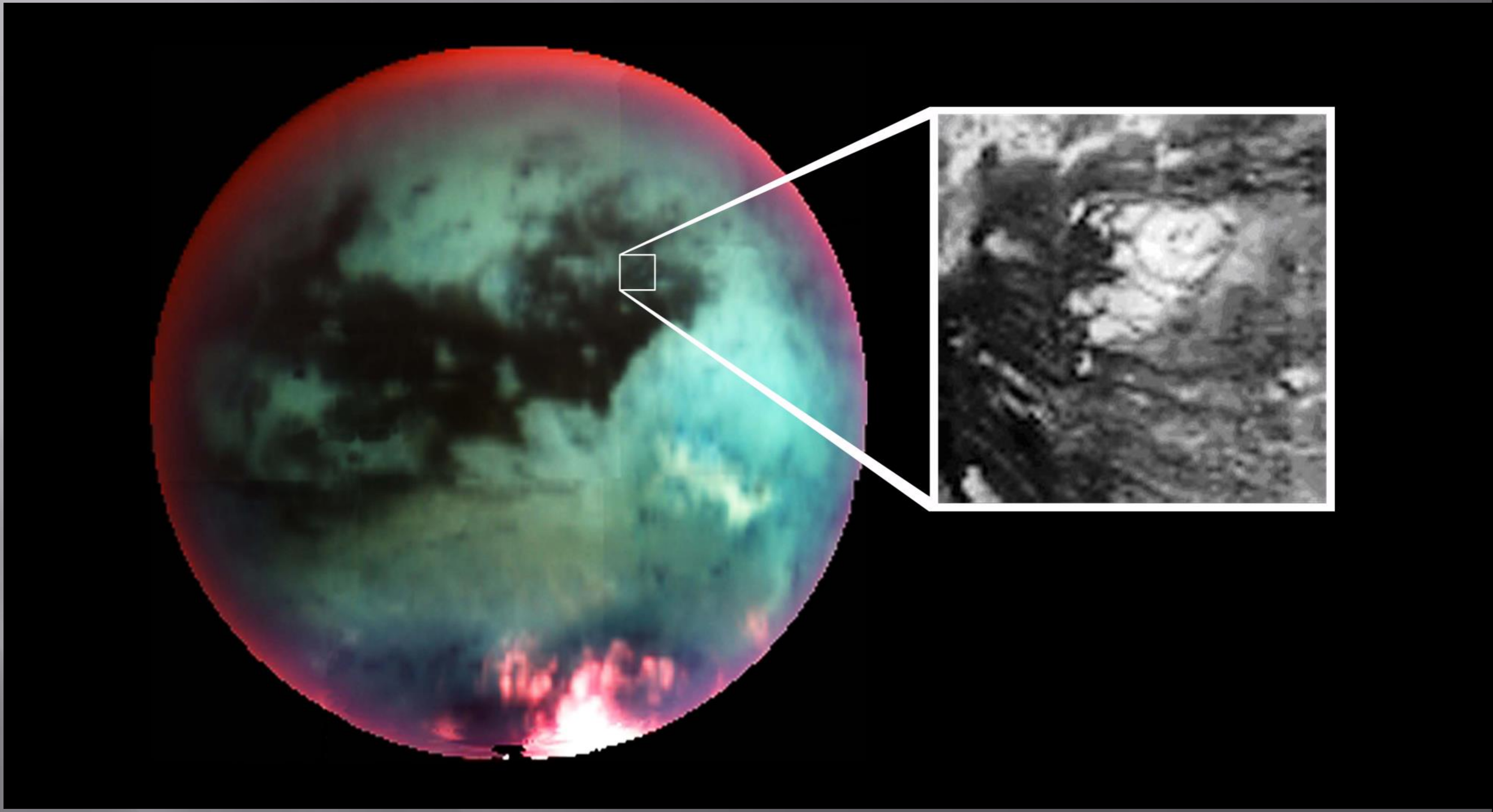


- Incident solar wind and electrical discharges provide the energy for in situ synthesis of the organic solids.

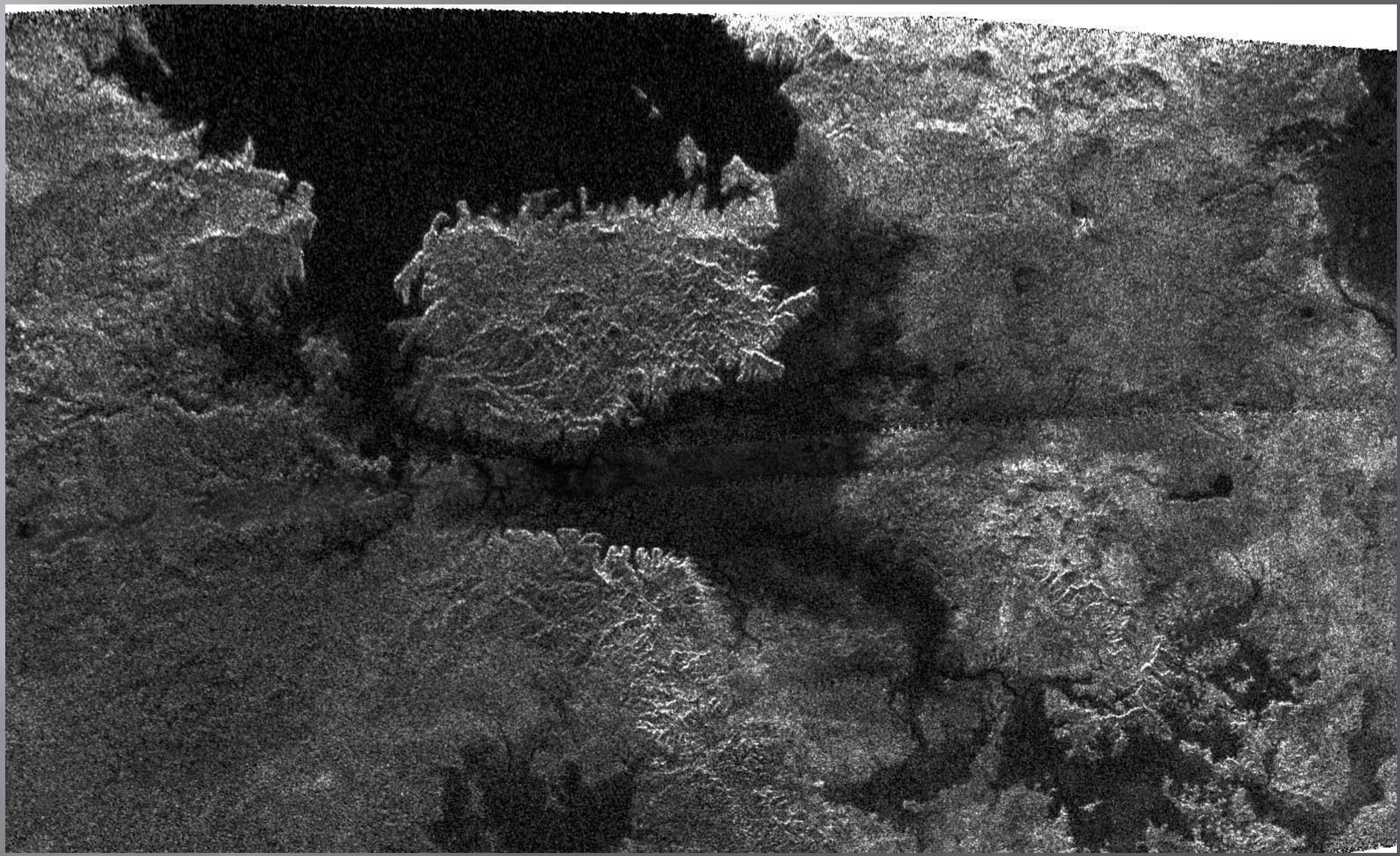
The Saturnian System: Titan (Planet Organica)

- Voyager I passed within 4934 km of Titan's surface on November 12, 1980.
- Photographs showed Titan to be shrouded in orange smog.
- The predominant gas turned out to be N_2 (95%) not CH_4 (4%).

- Surface of Titan is covered with channels caused by liquid methane-ethane flowing in the recent past.
- Lakes of methane-ethane have been found in the polar regions of Titan.
- Only world where the temperature and pressure conditions allow for an active methanological cycle as well as liquid methane-ethane on the surface.
- Methane and ethane on this exotic world form clouds and precipitate to form lakes.
- Ethane and methane are probably released via cryovolcanoes

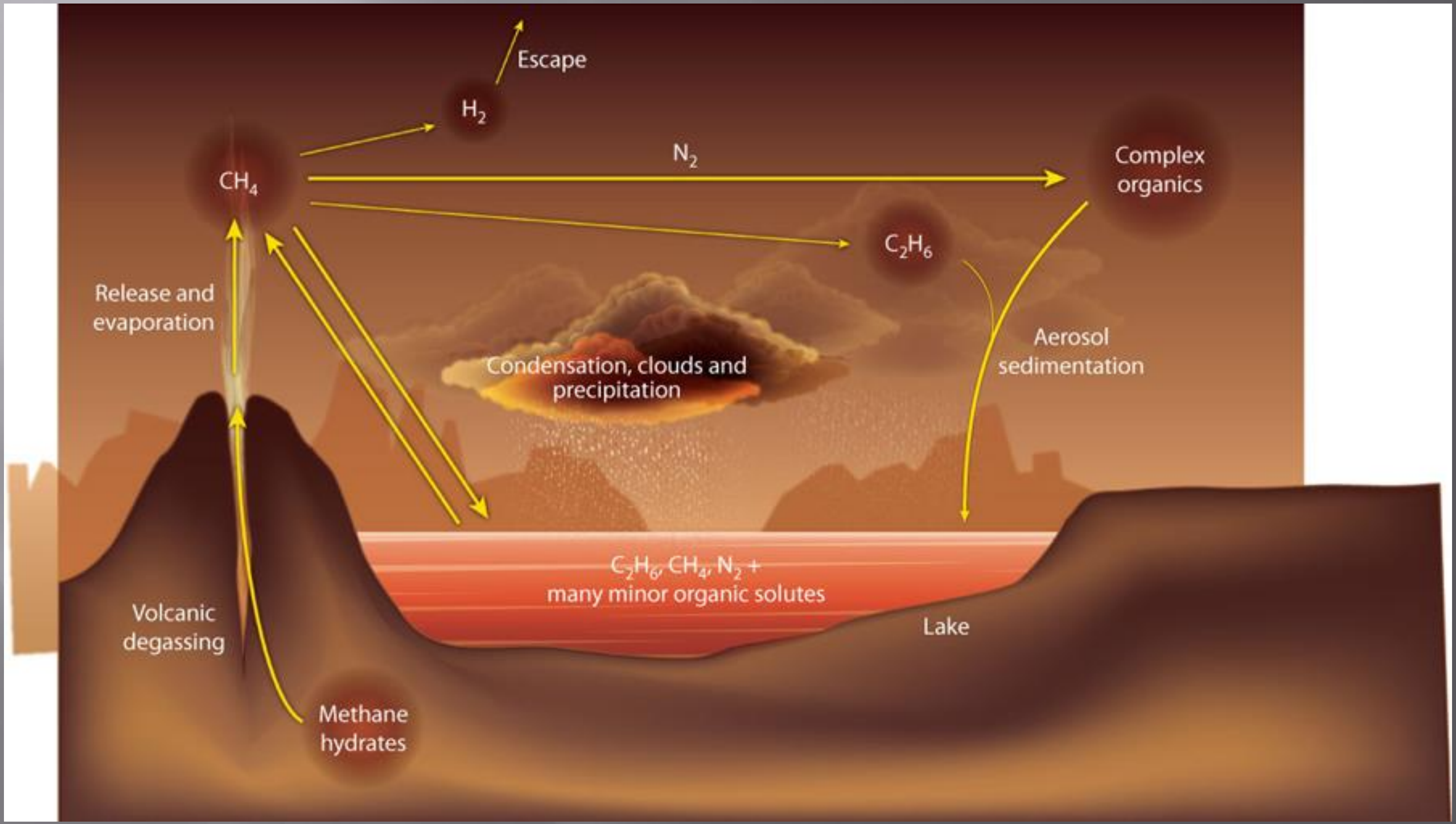


A cryovolcano on Titan

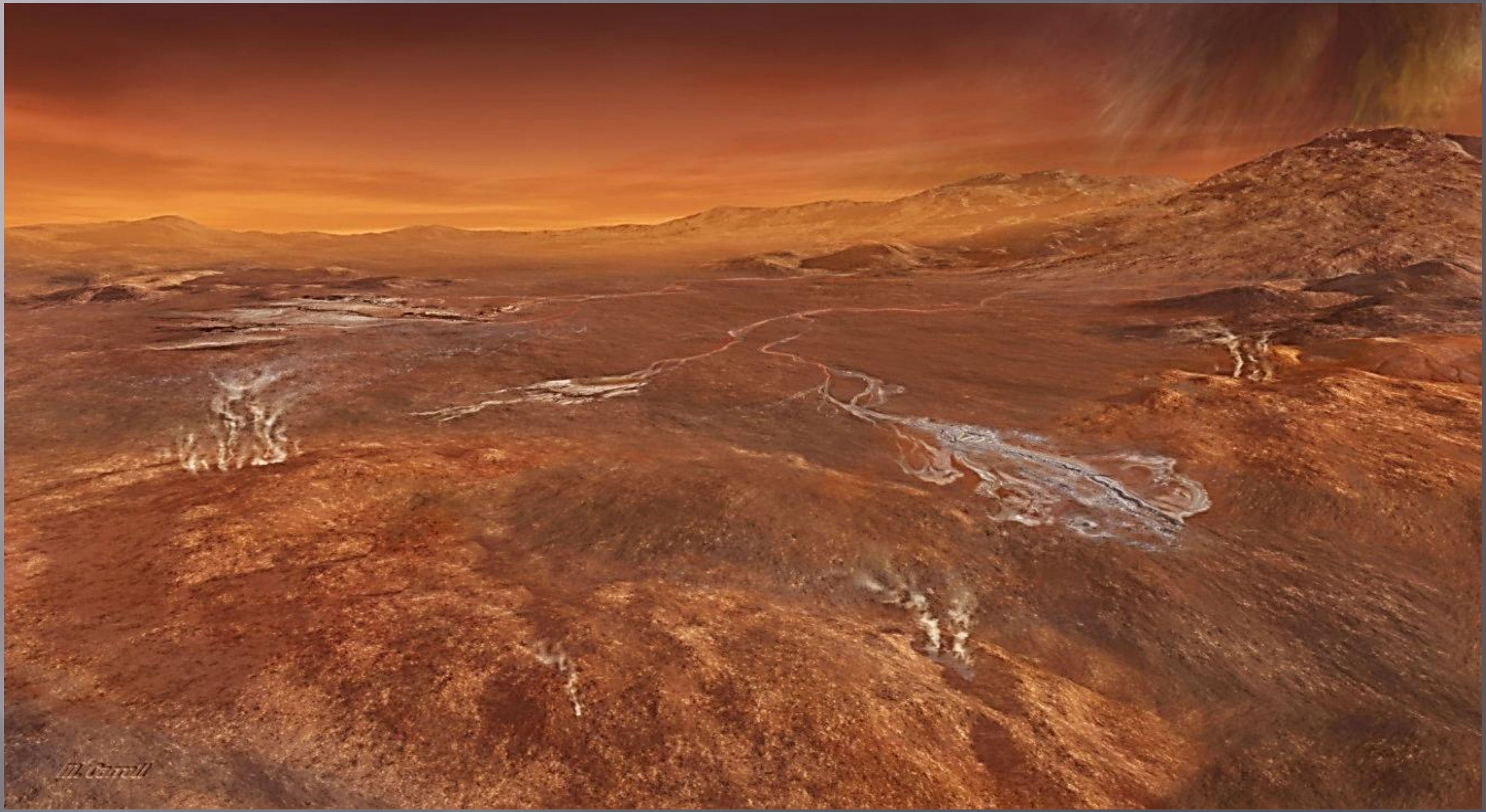


Radar image of methane-ethane lakes in Titan's northern hemisphere

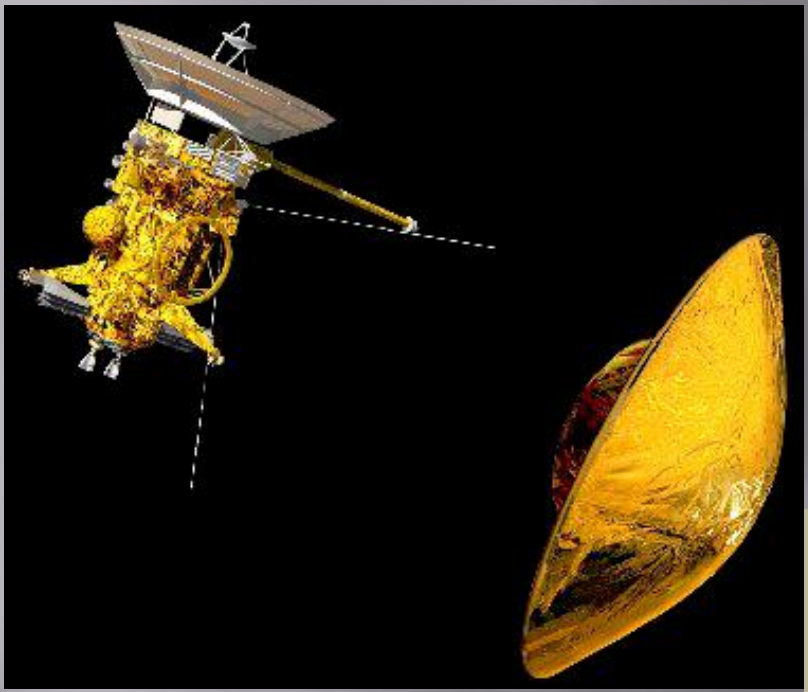
Titan's Methanolgical Cycle



- The result of the aerosol precipitation is a veneer of *tholins* that covers the entire planet!

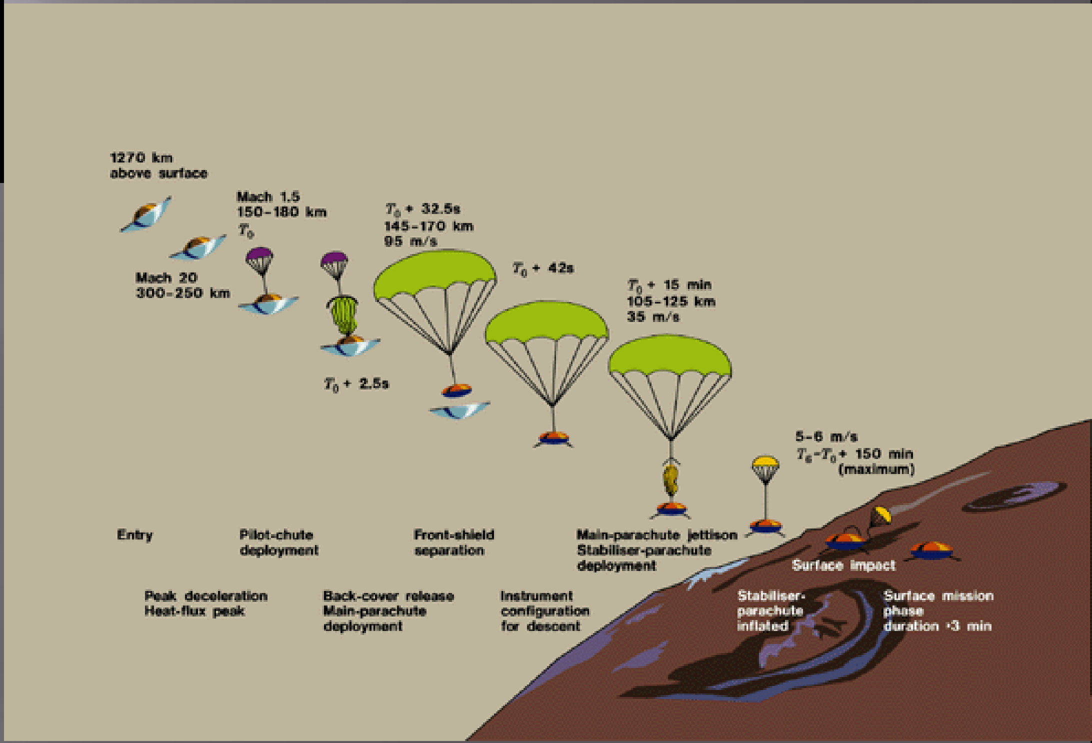


(artist's rendition)

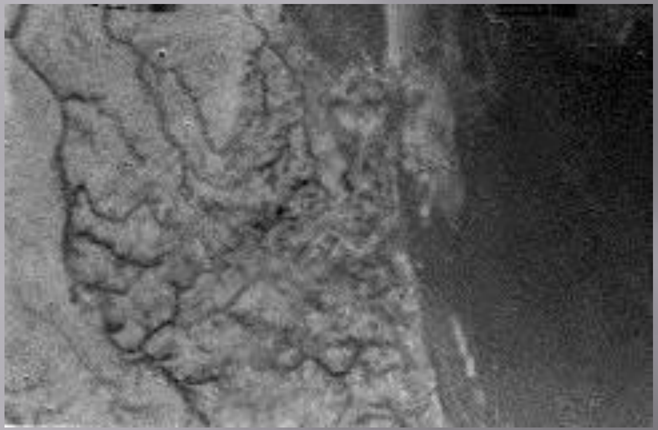


Release of Huygens probe: December 25, 2004

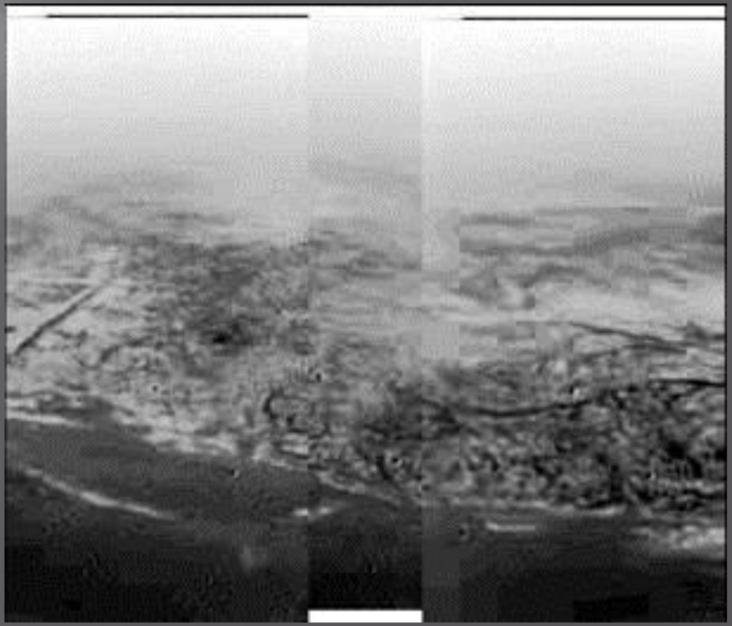
Huygens enters Titan’s atmosphere: January 14, 2005



First clear pictures of the surface of Titan

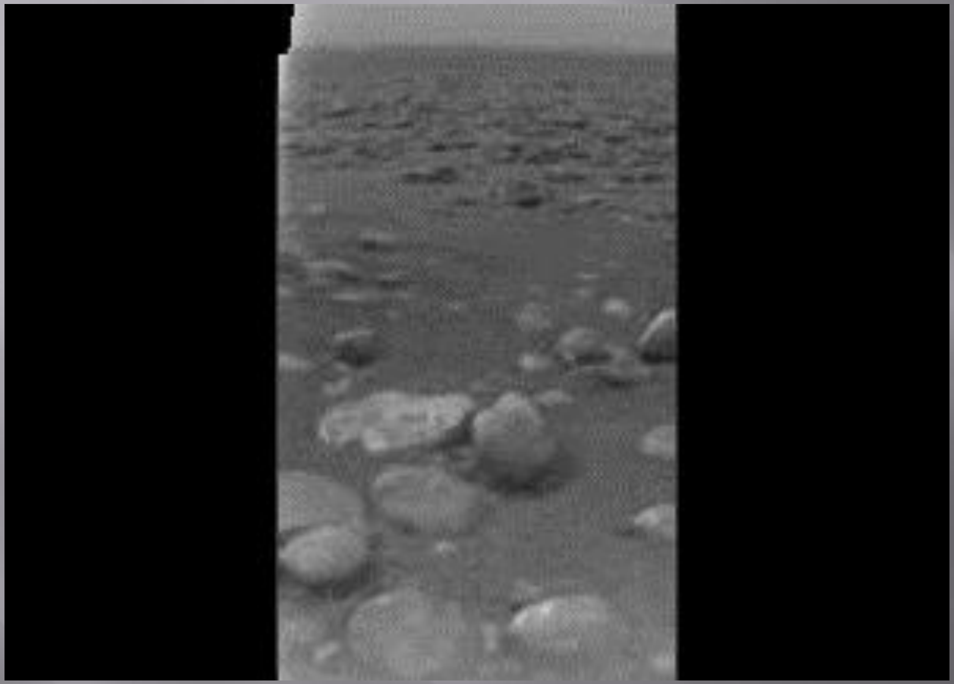


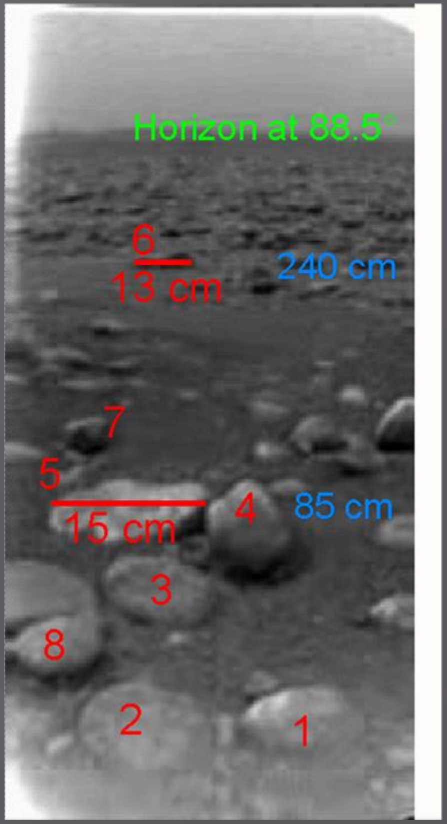
- 16.2 km altitude (40 m / pixel resolution)
- Dendritic structures flowing into a dark, flat region (drainage channels / shoreline)



- 8 km altitude; oblique angle (20 m / pixel)
- Higher, lighter coloured terrain and a low lying plain of dark material
- Reflectivity measurements indicate bright regions are water ice

Organic chemistry on a planetary scale!

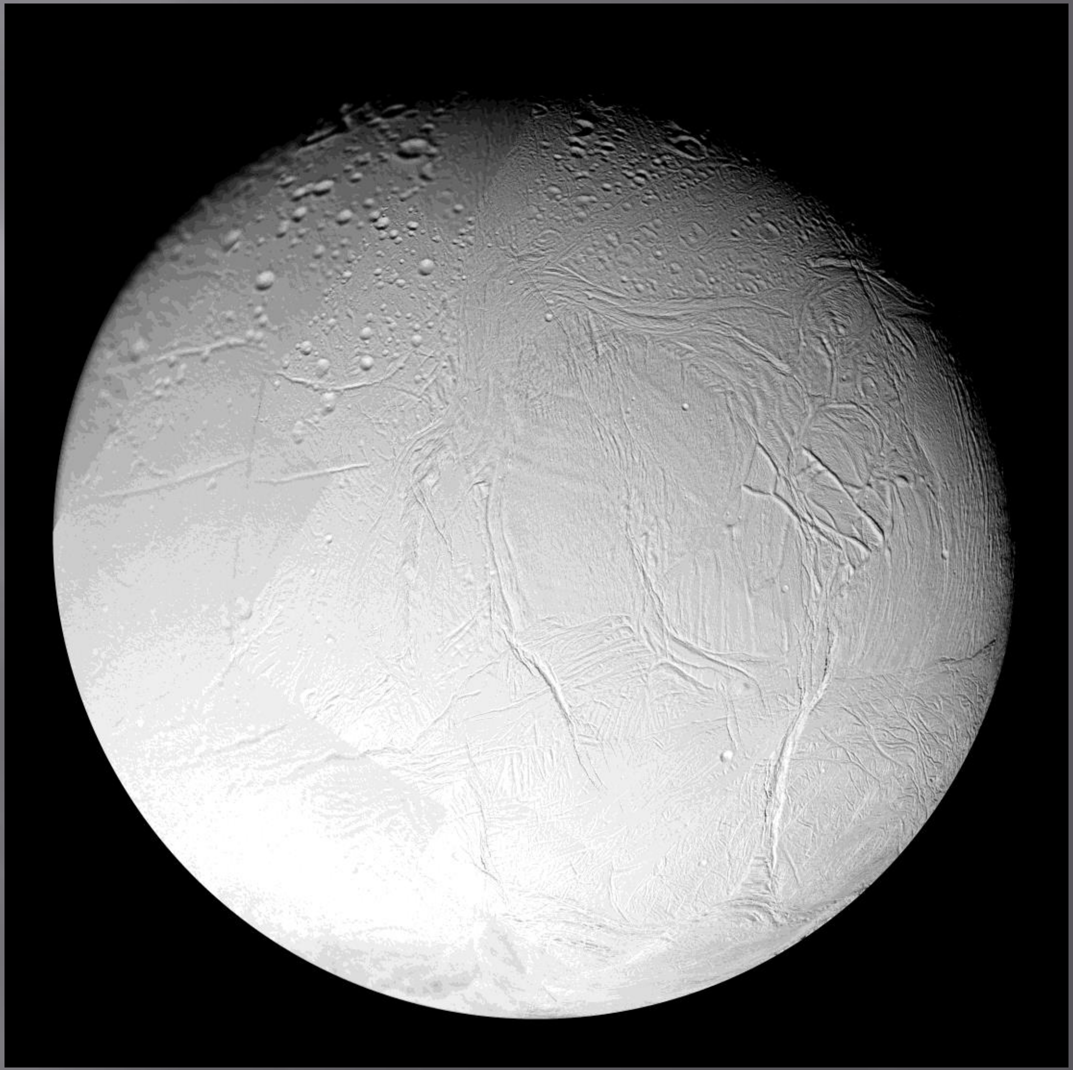




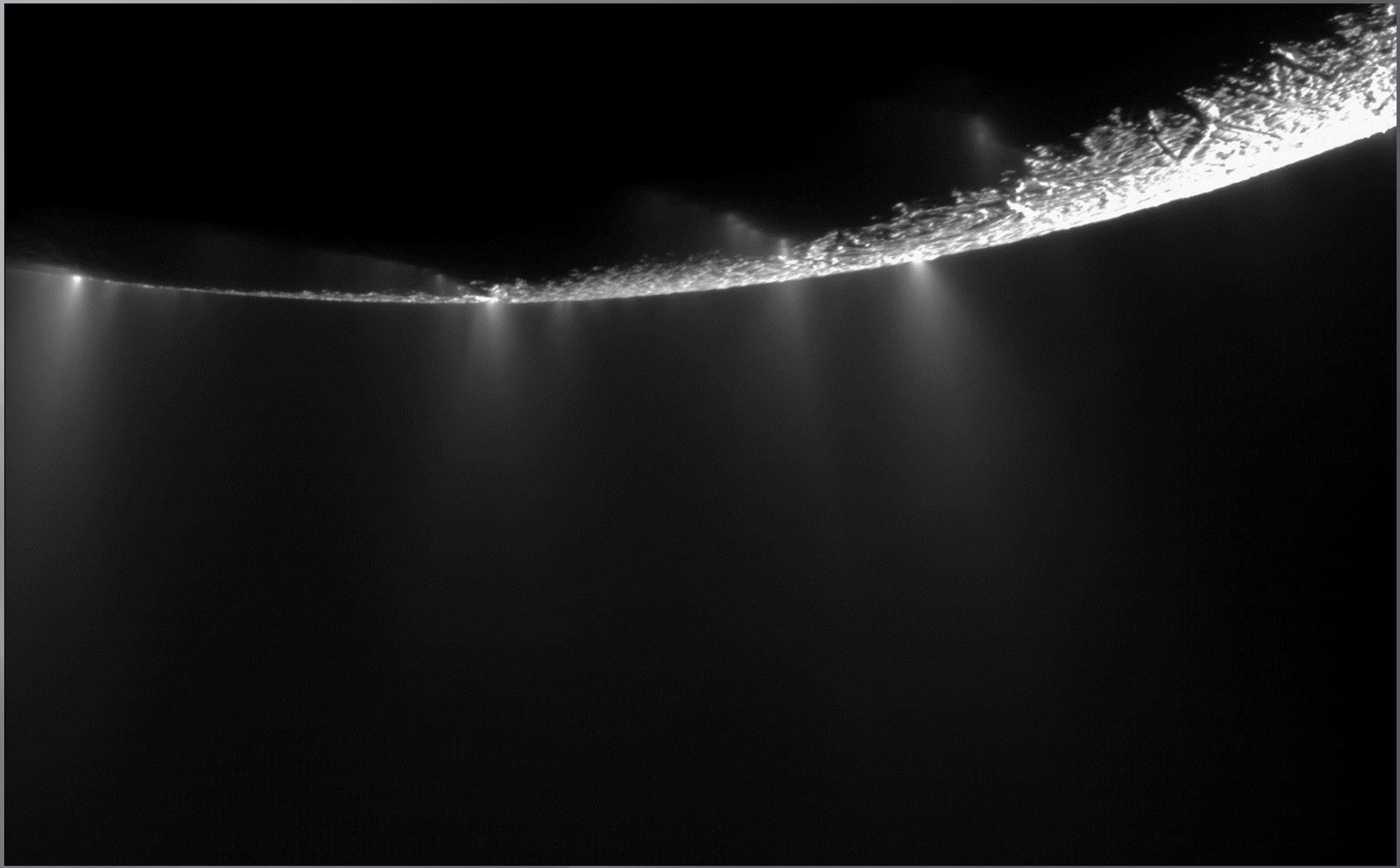
- Tholins and hydrocarbons cover water ice stones
- Methane fogged the camera lens

Enceladus

- Enceladus , a small moon in the Saturnian system (500 km diameter) is one of the most compelling bodies in the solar system.

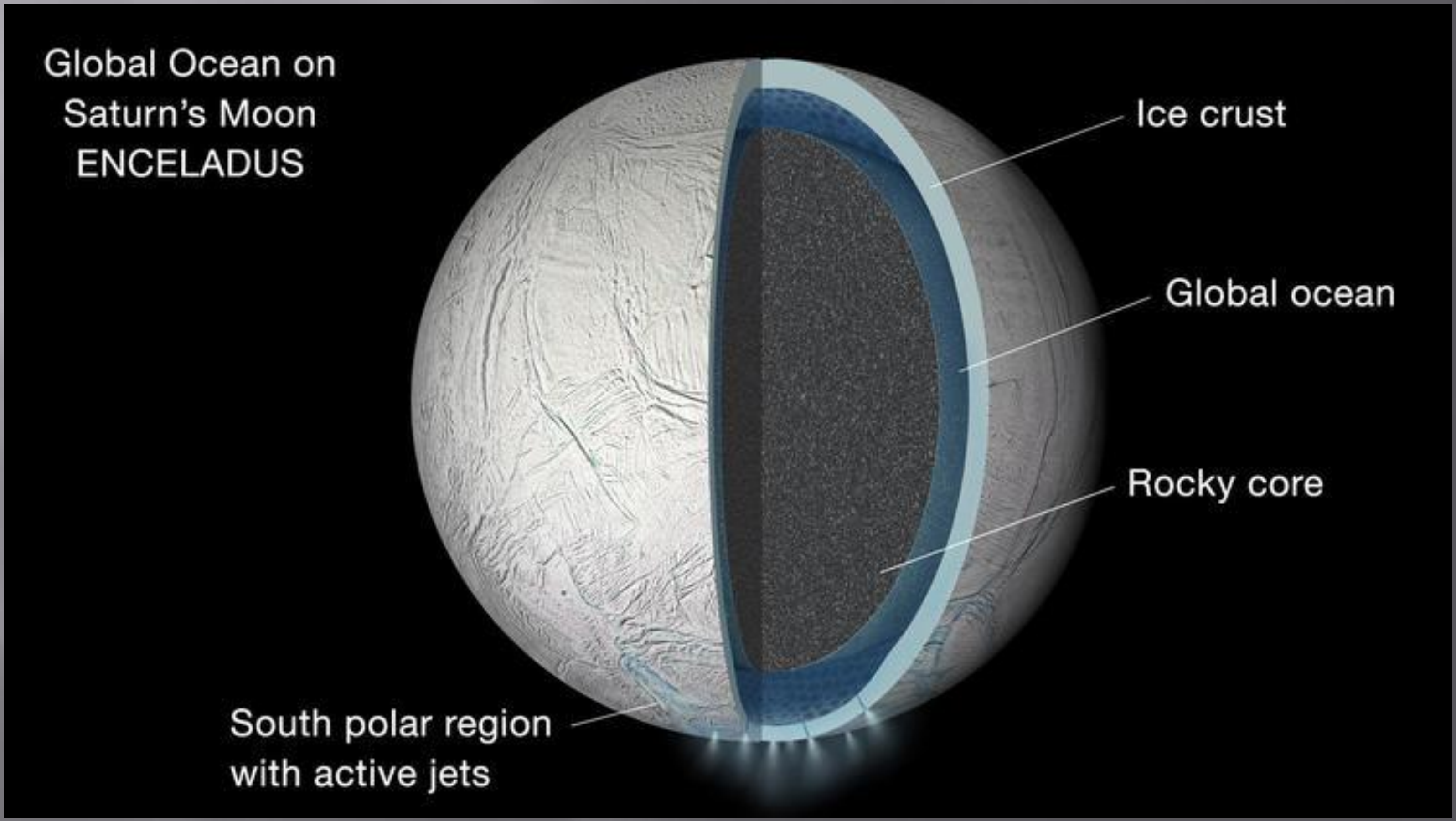


- In 2005, Cassini discovered it gushing water geysers into space.



- As Cassini dove through the plume of a geyser in 2015, it detected methane and formaldehyde.

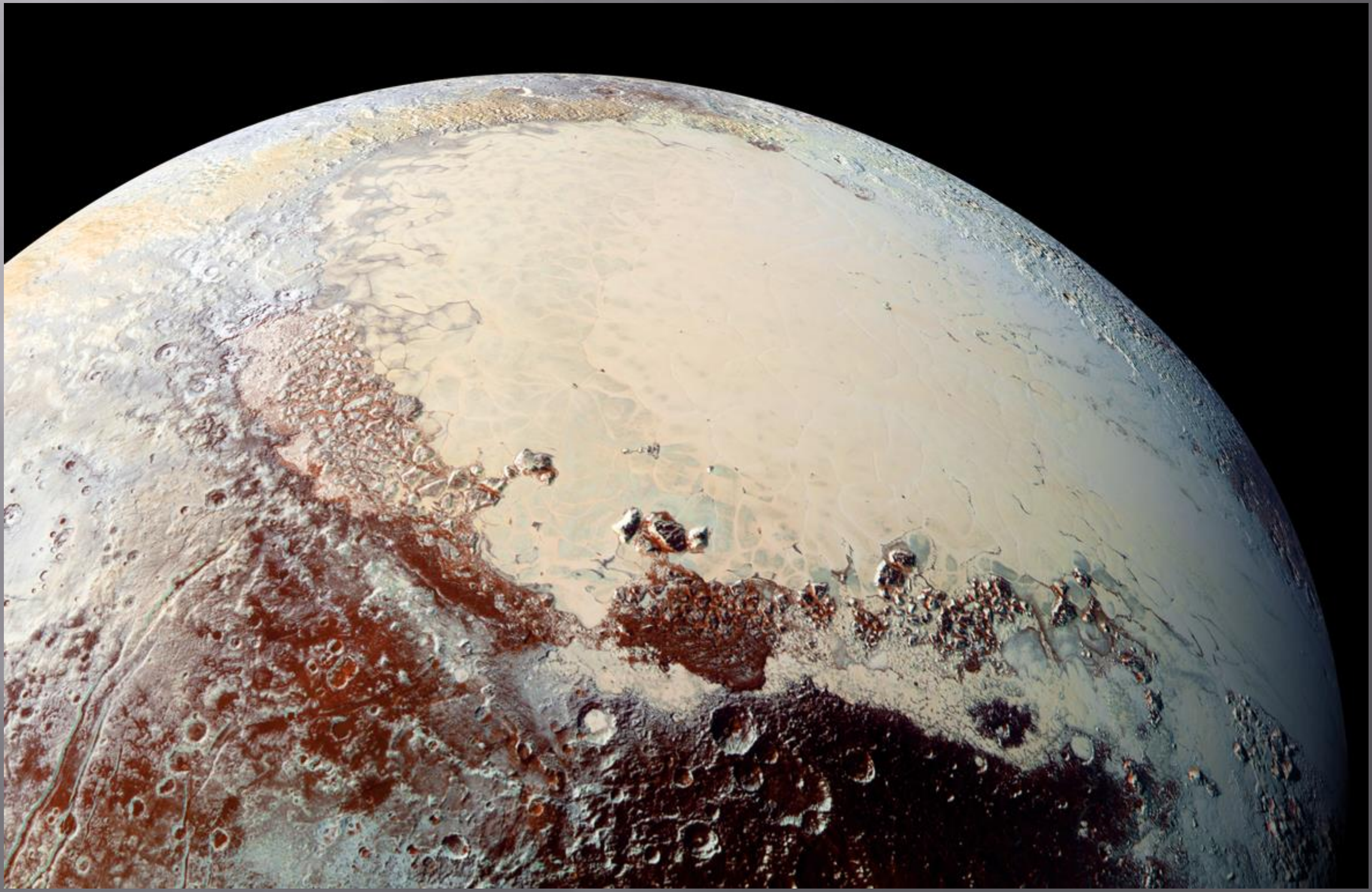
- These results suggest that there may be a salty sea beneath the icy surface that contains a mixture of pre-biotic organics.



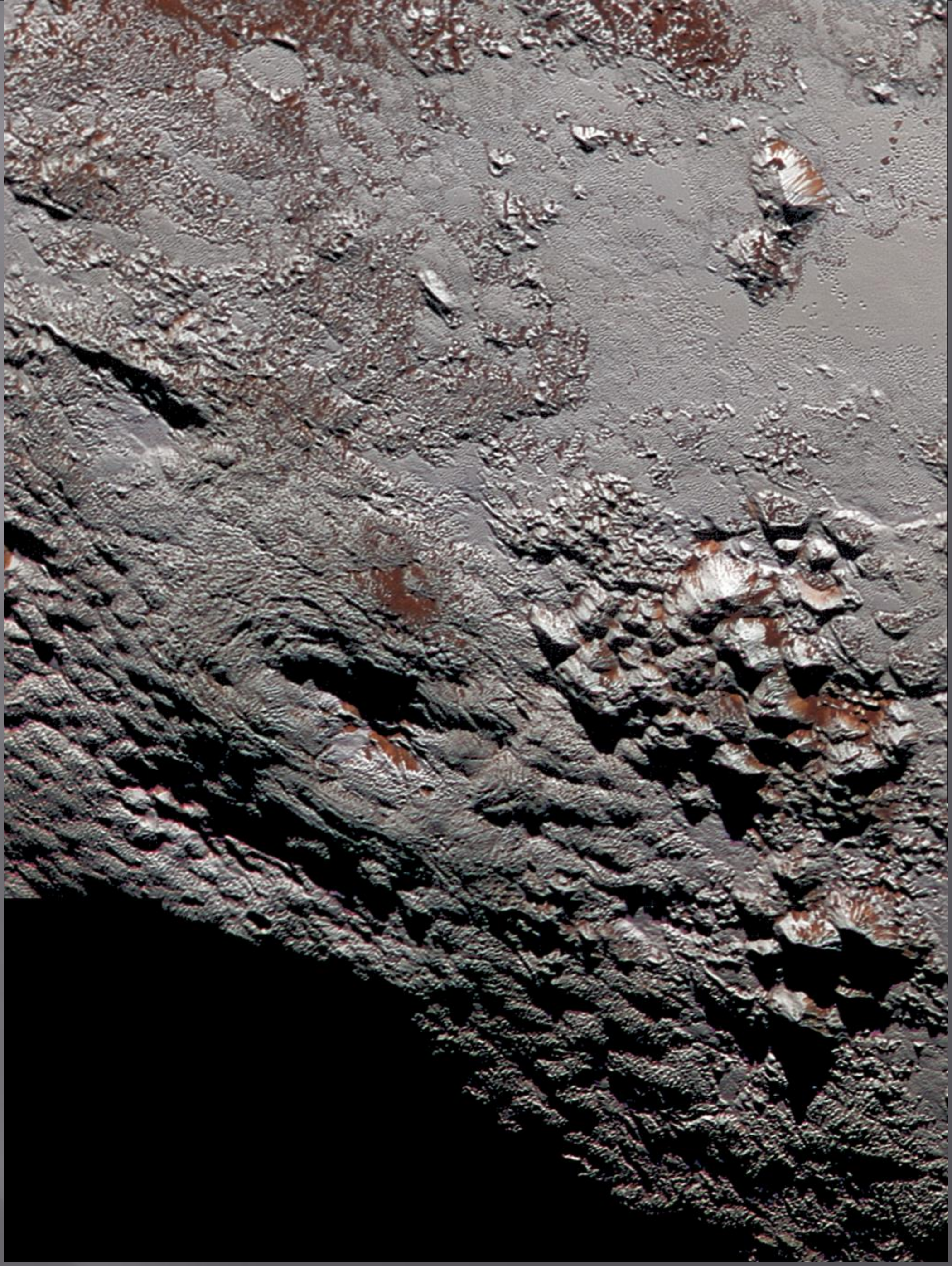
Pluto and Charon

- In 2015 the New Horizons spacecraft detected *tholins* on the surfaces of Pluto and Charon.
- Pluto's atmosphere is composed mostly of dinitrogen, but also contains some methane.

- The tholins on Pluto were probably created when cosmic rays and solar UV radiation interacted with the methane and dinitrogen in its atmosphere.



- New high resolution shot of Wright Mons , a dormant cryovolcano taken by New Horizons. (note the tholins on the flanks of the adjacent 3000-meter high water ice mountains)



- Some of Pluto's atmosphere has escaped and been trapped by Charon's gravity near its north pole.

- Reactions involving UV and cosmic rays then turned some of the constituents of the trapped atmosphere into tholins.

Comets

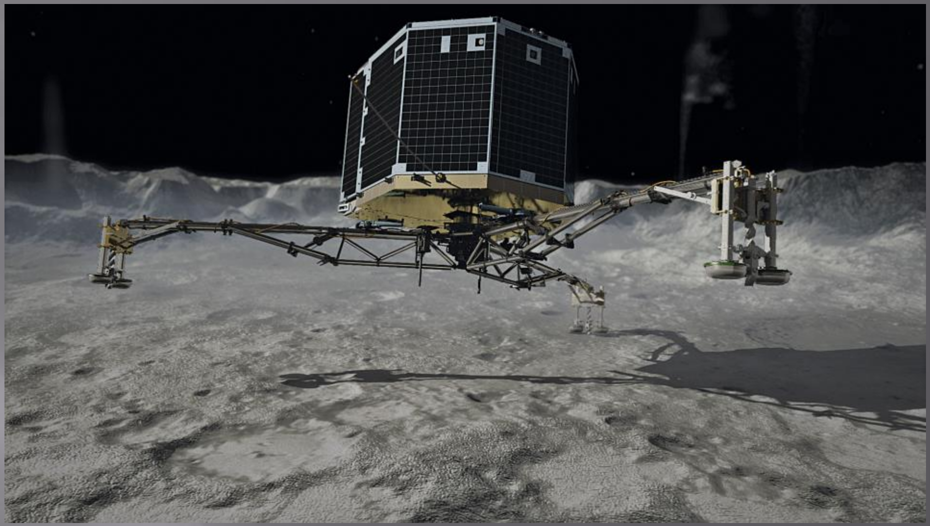
- Comets contain a higher percentage of first-generation interstellar organics than meteorites.
- Secondary processing does not occur because the interiors of comets do not get hot enough for liquid water to form.
- The populations of organics in comets are chemically "simple," showing a smaller variety of structural types and classes of organic compounds than typically seen in meteoritic organics.

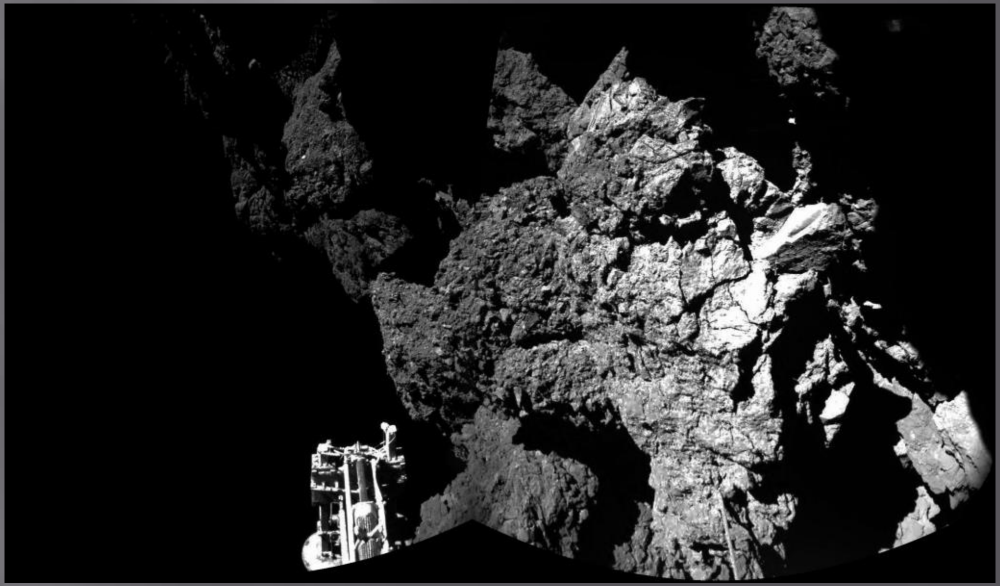
- E.g. 14 simple organic compounds, the majority of which are probably original organics swept into our solar system 4.57 billion years ago, were detected by the Philae lander which alighted on comet 67P in 2015:

Comet 67P

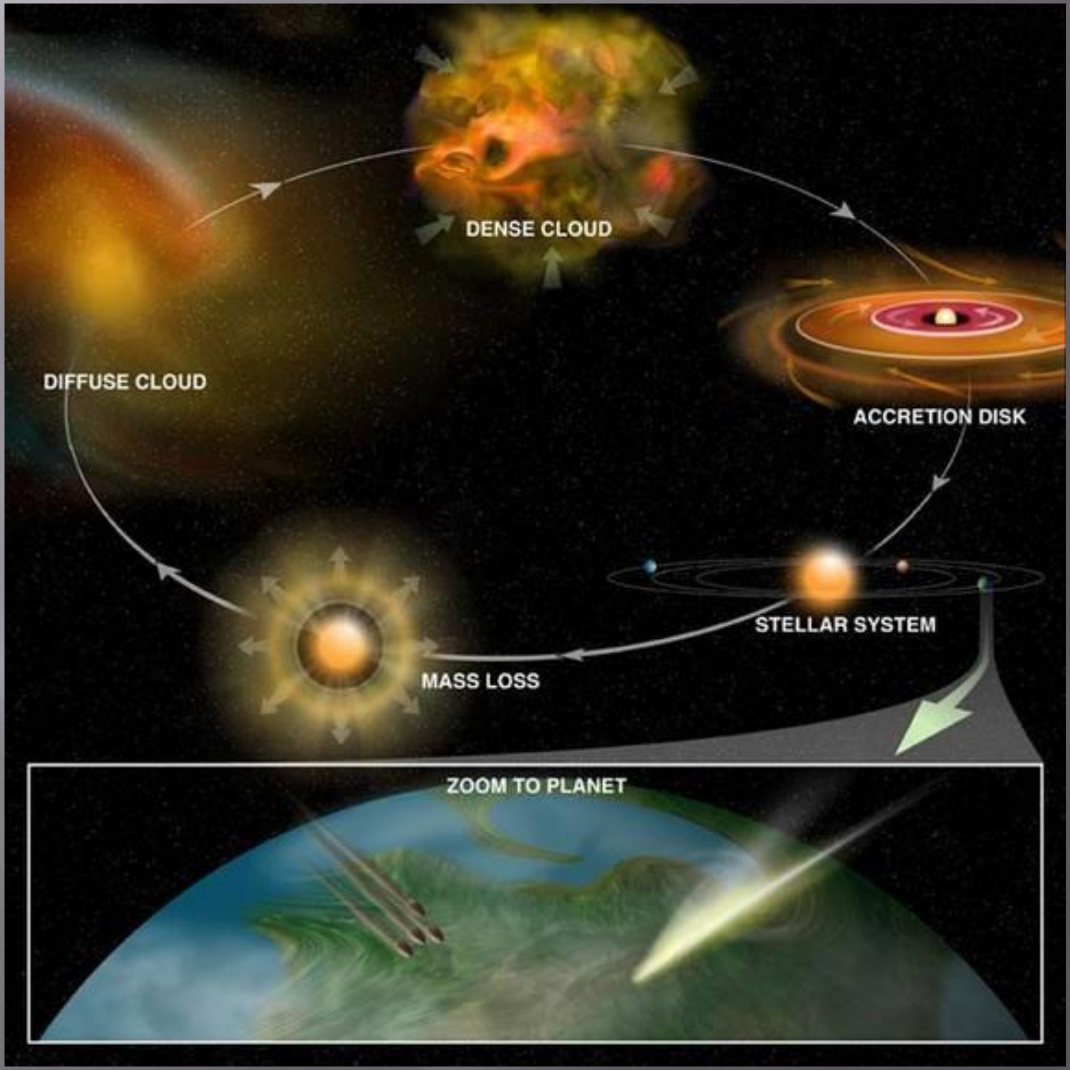
Compounds found by Philae

Methane
Hydrogen cyanide
Carbon monoxide
Methylamine
Acetonitrile
Isocyanic acid
Acetylaldhyde
Formamide
Ethylamine
Methyl isocyanate
Acetone
Propionaldehyde
Acetamide
Ethylene glycol





Extraterrestrial Compounds in Our Solar System: Origins and Parent-Body Alterations: A Summary



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