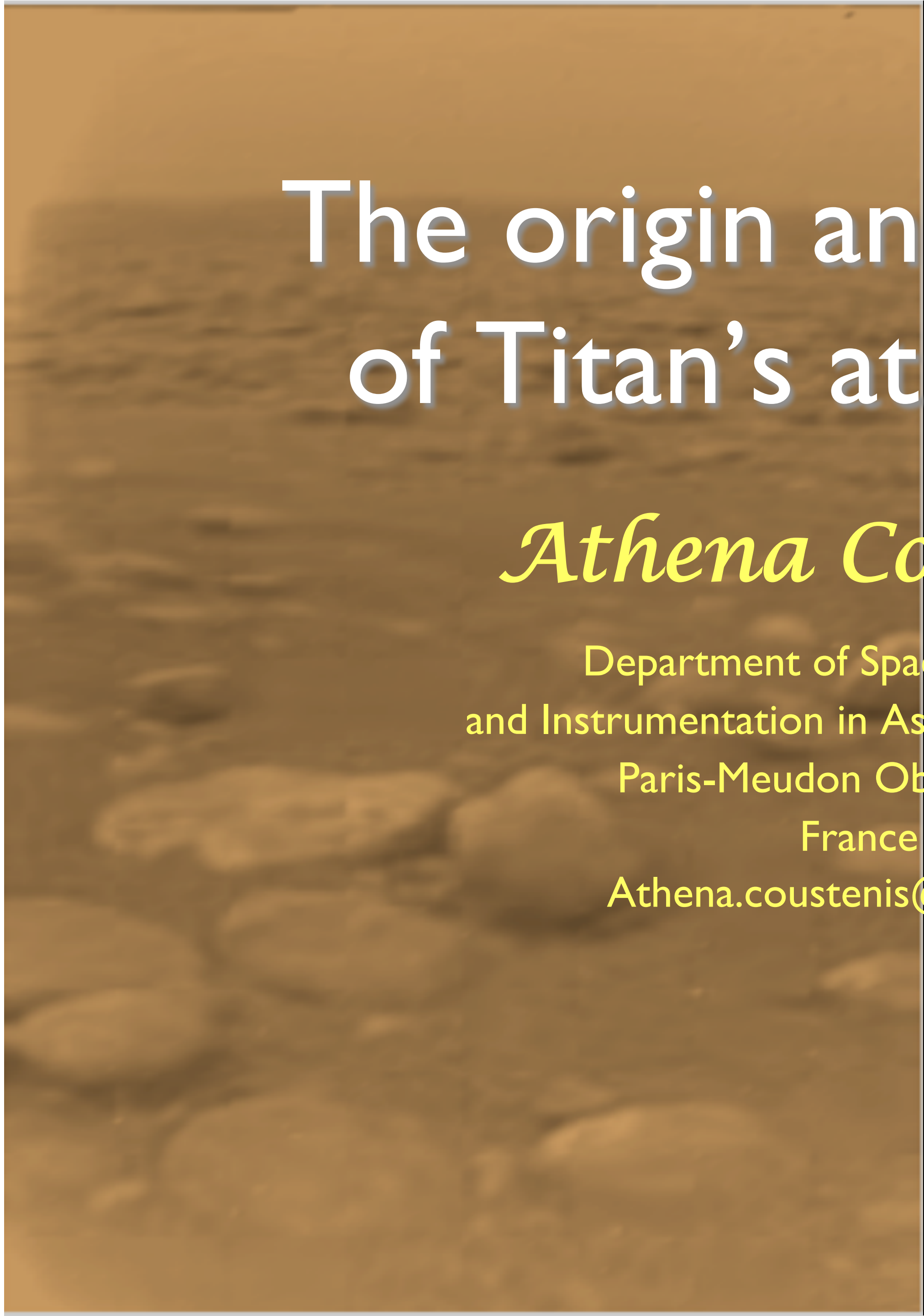

The origin and evolution of Titan's atmosphere

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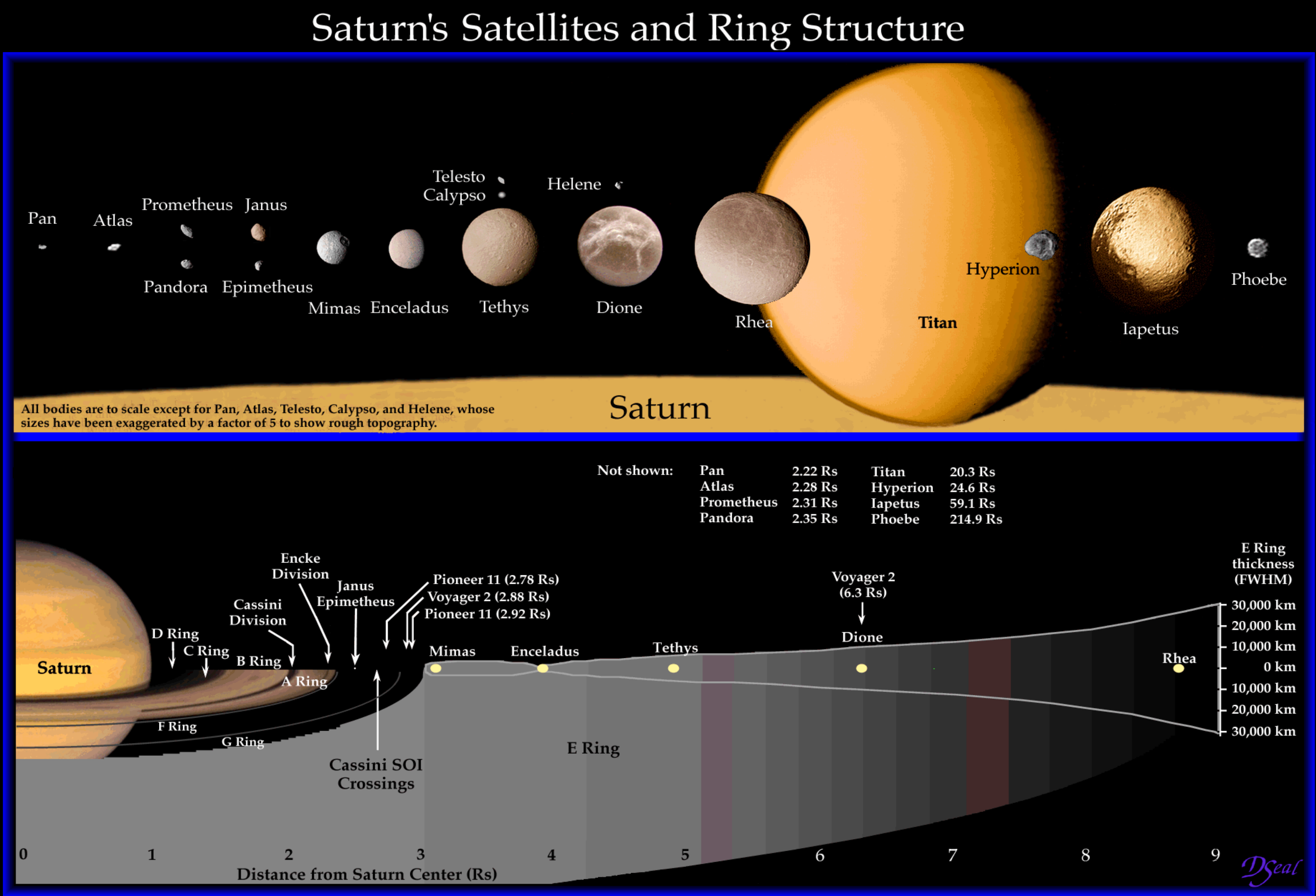
Saturn's satellites



This graphic is available in color if required.

Titan Through Time

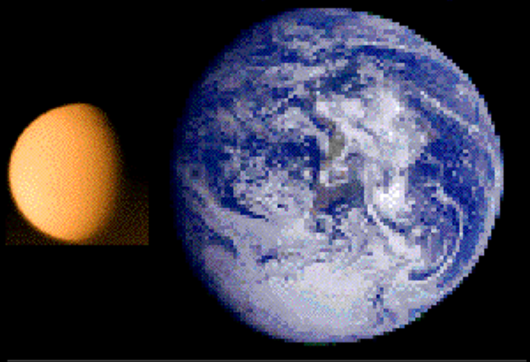
- Christianus Huygens discovers Titan, 1655
- Ground-based :
  - atmospheric limb darkening (Comas Solas, 1908)
  - CH_4 detected (Kuiper, 1944)
- Voyager (1980)
  - mean distance from Saturn = 1,211,850 km (~ 3.1 x Earth-Moon distance)
  - orbital period= 15.94 days (Earth's moon 27.3 days)
  - N_2 detected as main component, CH_4 second most abundant (Voyager, 1980)
  - mass = 1.35×10^{23} kg (0.023 x Earth's)
  - radius = 2575 km (0.98 Ganymede; 1.48 x Moon; 0.76 x Mars)
  - mean density = 1.88 g/cm^3 (50% ice, 50% rock)
  - mean surface temperature = 93.5 K (-179.5 °C, -291 °F)
  - atmospheric pressure = 1.5 bars
  - atmospheric density = 4.4 x Earth's atmosphere
- Ground-based and Earth-bound observatories (HST, ISO) – 1990s
  - Heterogeneous surface
  - Interesting atmospheric phenomena
- Cassini arrives at Saturn on 30 June 2004
- Huygens lands on Titan 14 January 2005
  - Ouaouh!

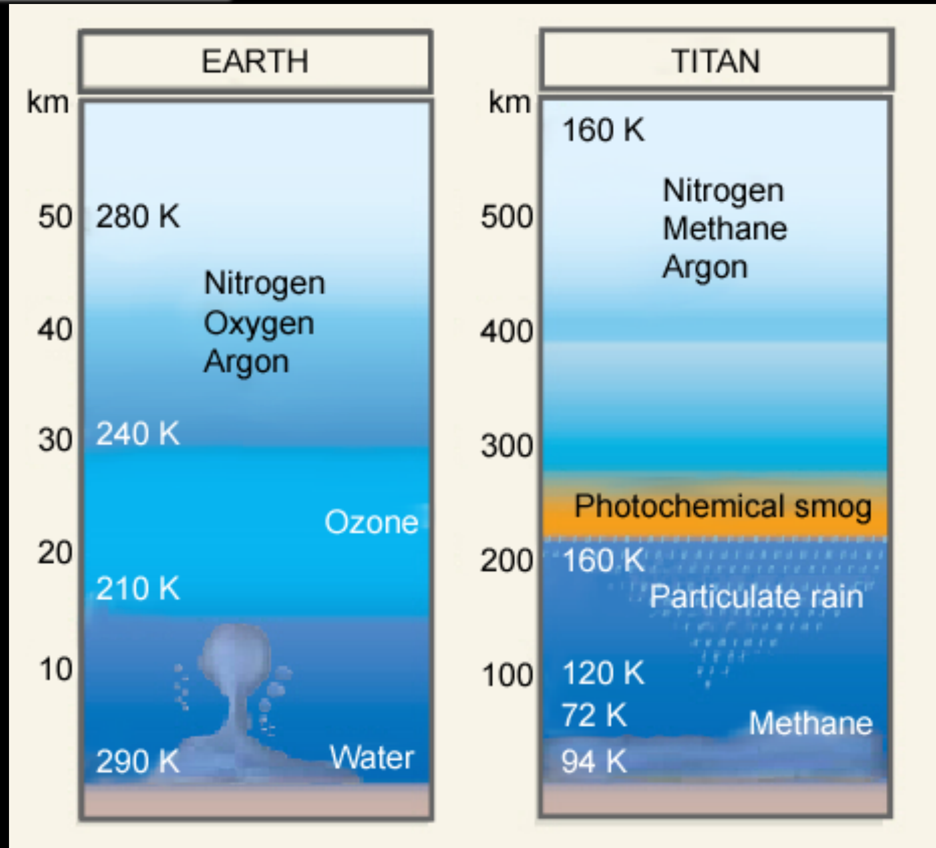
Characteristic	Ganymede	Titan	Enceladus	Triton	Pluto
R_{planet}	14.99 R_J	20.25 R_S	3.95 R_S	14.33 R_N	[39.53 AU]
M [10^{22} kg]	14.82	13.5	0.011	2.14	1.31
R_e [km]	2631	2575	252	1352	1150
ρ [kg/m^3]	1936	1880	1608	2064	2030
g [m/s^2]	1.43	1.35	0.12	0.78	0.4
T_O [days]	--	--	--	--	[248.5 yr]
T_S [days]	7.16	15.95	1.37	5.877	[6.38]
i [deg]	0.18	0.33	0.02	157	17.14
e	0.001	0.029	0.005	0.000	0.25
A	0.4	0.2	1.4	0.4	0.52
v_e [km/s]	2.75	2.64	0.235 *(< v_T !)*	1.50	1.1
Surface T [K] P	110 X	94 1.5 bar	114-157	38 16 μb	40 58 μb (var)
Atmosphere	O_3, *(H_2O_2-i)*	**N_2**, CH_4	H_2O, **N_2**, CH_4, CO_2, CO	**N_2**, CH_4	**N_2**, CH_4, *(H_2O-i)*

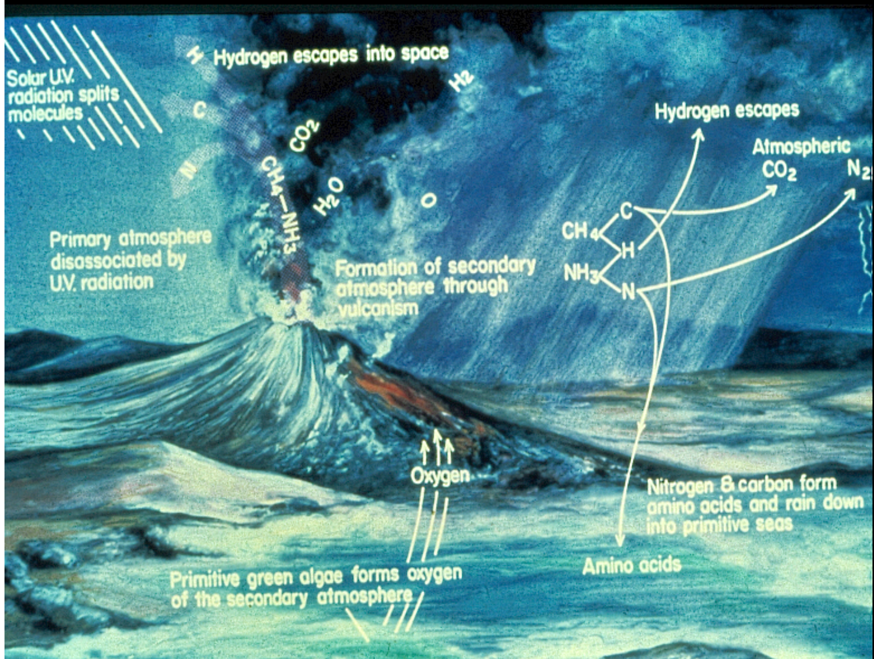
TITAN: WHY ARE WE INTERESTED?

- It is of general interest to the study of chemical evolution:
  - N_2, CH_4 and other abundant organic gases (nitriles and hydrocarbons) are present in the atmosphere
  - An orange-brown cloud deck globally covers the satellite, in which aerosol layers and, methane/ethane clouds are also present.
  - The products of atmospheric chemistry may have been preserved over all of Titan's history.
  - The surface has a pressure of 1.5 bar and hosts several complex features like Earth (dunes, lakes, volcanoes, channels, etc) but with different actors/materials.
- Conditions on Titan are not identical to those on Early Earth:
  - The temperatures are too low in the atmosphere (70-200 K) and on the surface (T~94 K), where liquid water is absent
  - The composition of the atmosphere is different (CH_4-N_2 vs CO-CO_2-N_2) with very little oxygen
  - Methane cycle vs water cycle
  - The solar UV radiation is only about 1% of that at the Earth
  - The infall of carbonaceous material is smaller today than in the past

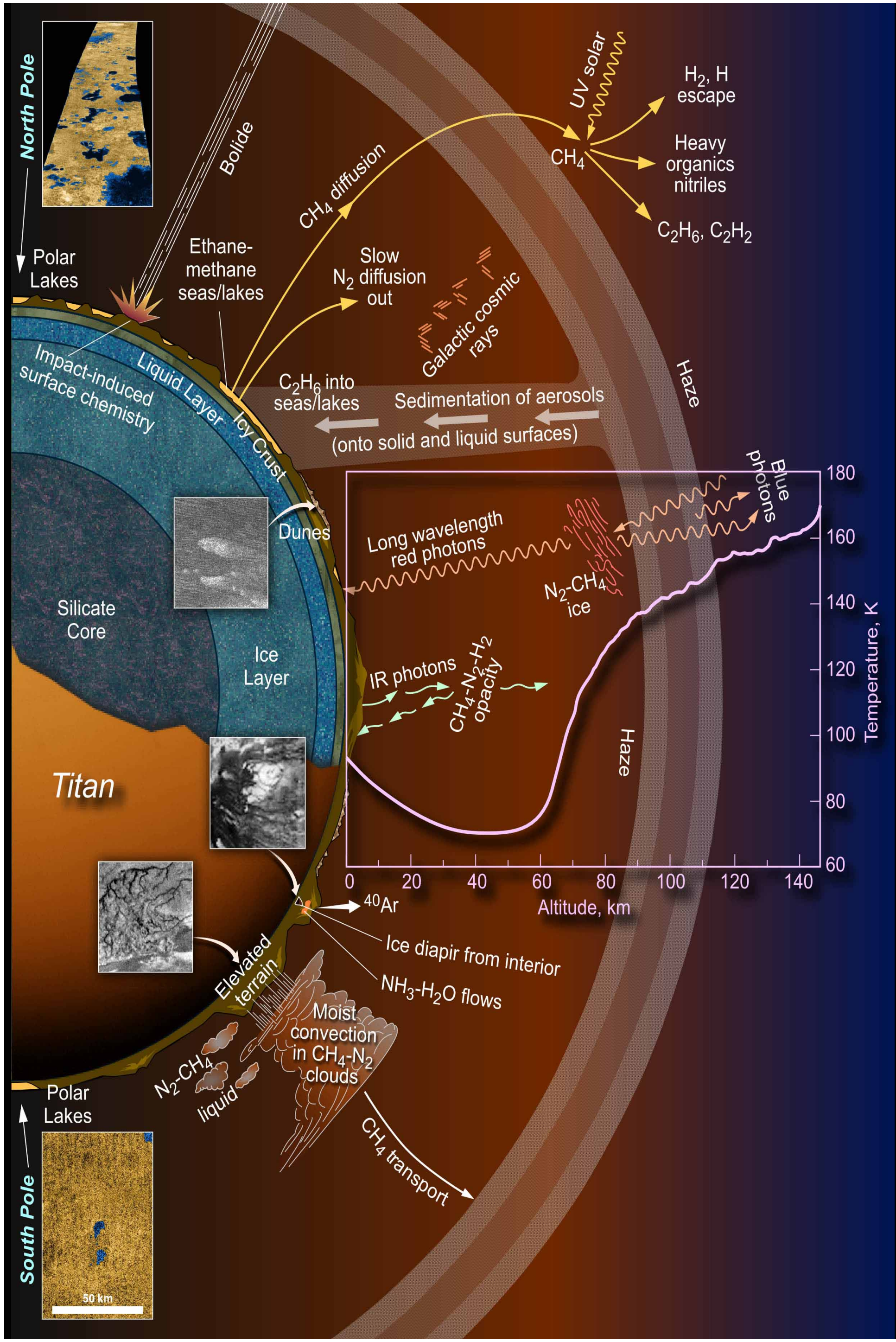
Titan and the Earth







Titan provides a good analogue as a natural laboratory in which chemical and physical processes can be studied on a planetary scale and help us understand early chemical evolution in the primordial atmosphere on Earth



- Thick and extended atmosphere mainly composed of N2 (97%) and CH4 (1.5%), surf T= 94K, surf P= 1.5 bar
- Intense and complex chemistry {C, H, N, O} leading to hydrocarbons, nitriles and oxygen species
- In Titan's conditions, CH4 and C2H6 can condense and produce clouds, haze and surface liquid
- Exotic climate: hydrocarbon cycle, analogous to Earth's hydrological cycle producing clouds, rain, lakes…
- The surface looks familiar but with different material and shaped by weather, with lakes/seas, dunes, channels

- What is the nature and distribution of methane sources?
- Differences between the tropical and polar climate?
- What is the seasonal evolution of the methane cycle?
- What is the seasonal/secular equilibrium and transport of liquid and haze?

Origin of Titan's atmosphere

a mystery: why does Titan also have a large nitrogen atmosphere?

Questions remain

Where does Titan's atmosphere come from?

- nitrogen ?
- methane ?

Composition of ices produced in the solar nebula: a recipe

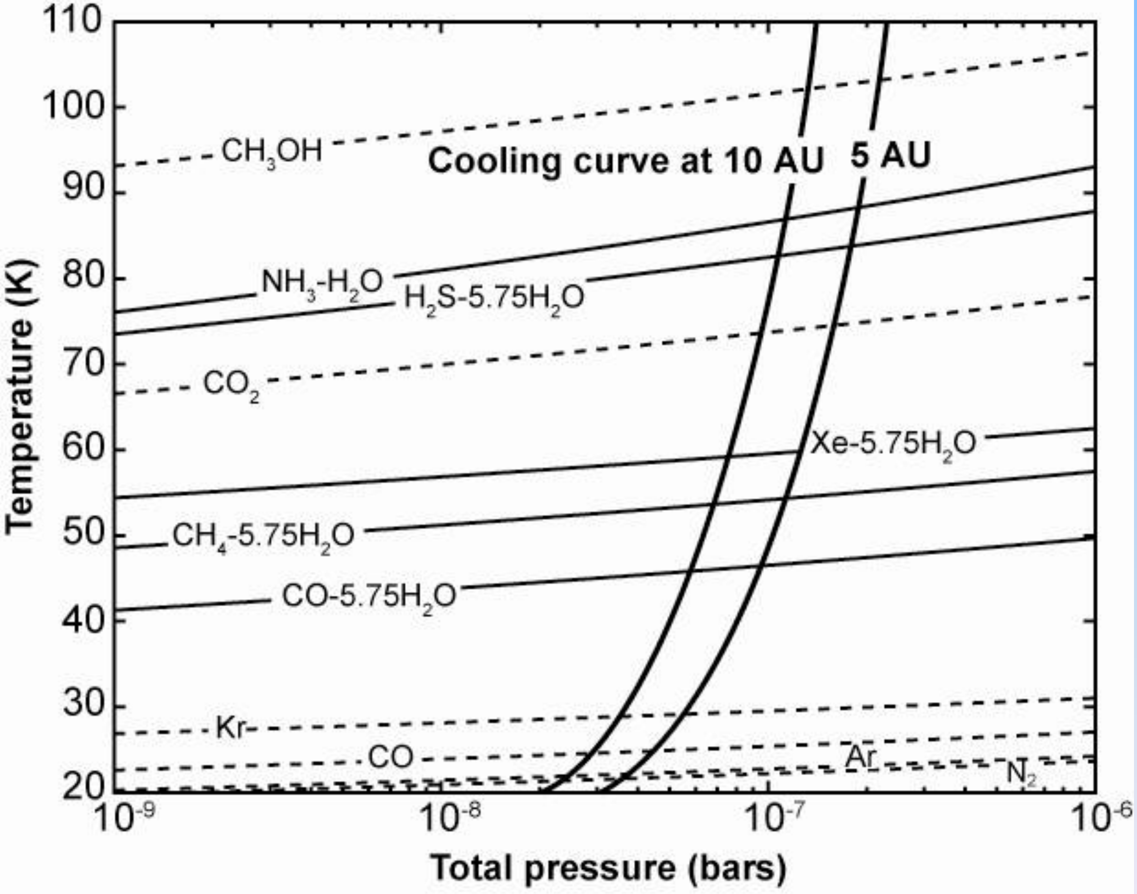
➡ ***What relative quantities of different species are included in icy planetesimals?***

- **Ingredients**
  - Thermodynamic conditions in the ***protoplanetary disc*** (*P*, *T*, Σ)
  - ***Initial gas-phase*** molecular composition
  - ***Stability curves*** of the different ices

- **General assumptions**
  - Focus on regions beyond the snow line
  - Number of species limited to H_2O, CO, CO_2, CH_3OH, PH_3, CH_4, N_2, NH_3, H_2S, **Ar, Kr and Xe**

Formation of icy planetesimals in the primordial nebula assuming a solar abundance for all elements

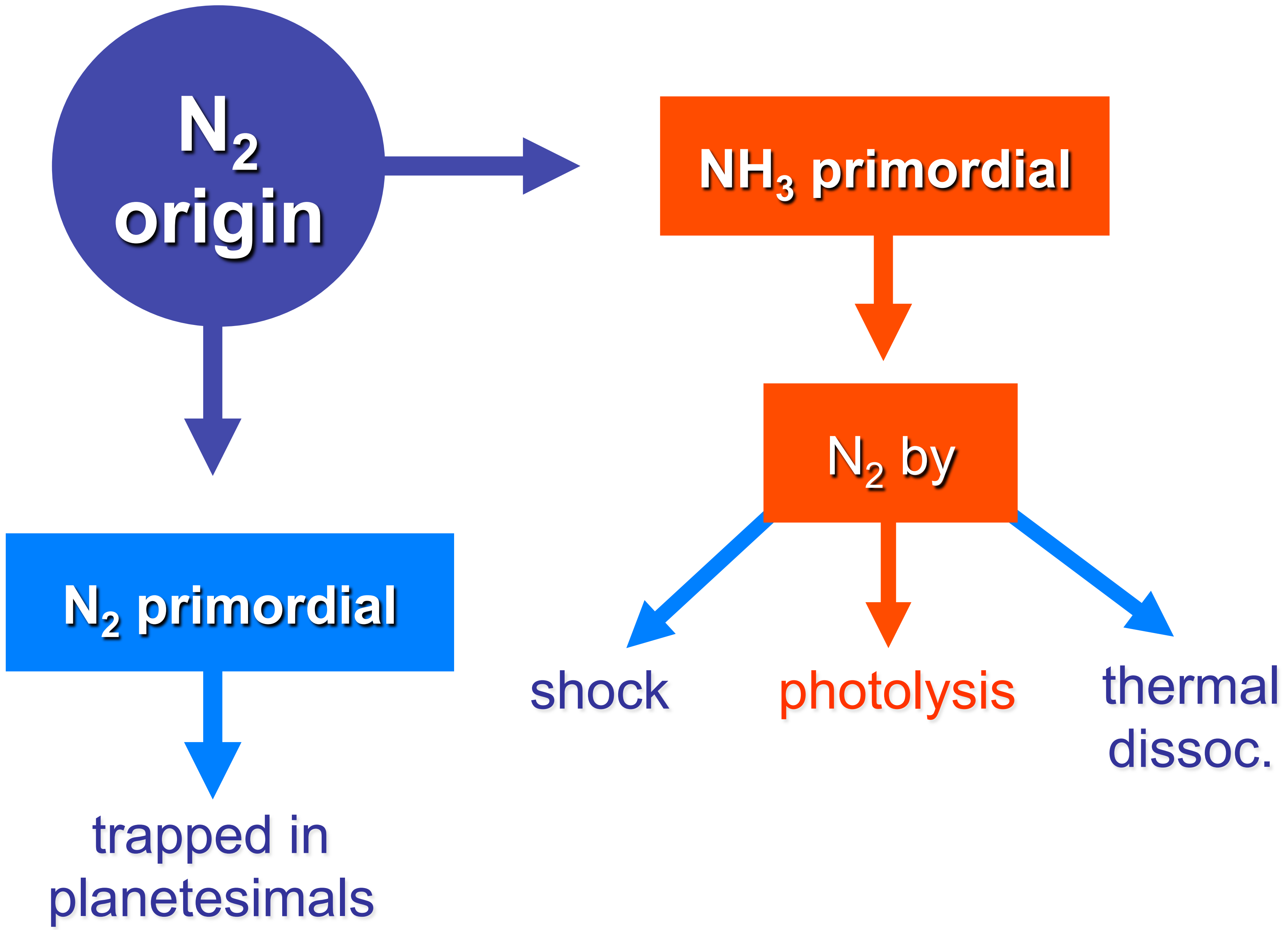
CO:CO2:CH3OH:CH4 = 70:10:2:1 and N_2:NH_3 = 1:1 in the gas phase



Formation of clathrates and pure condensates in the outer solar nebula

condensation /trapping

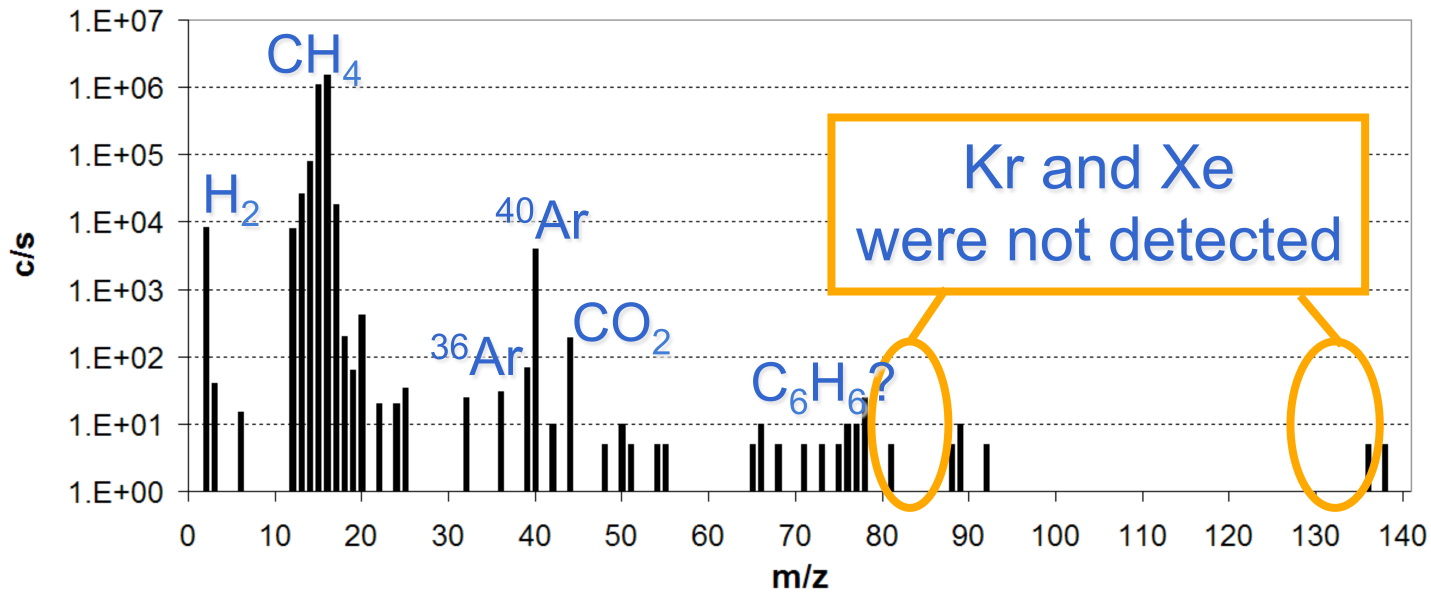
accretion



N_2 origin
NH_3 primordial
N_2 by
N_2 primordial
shock
photolysis
thermal dissoc.
trapped in planetesimals

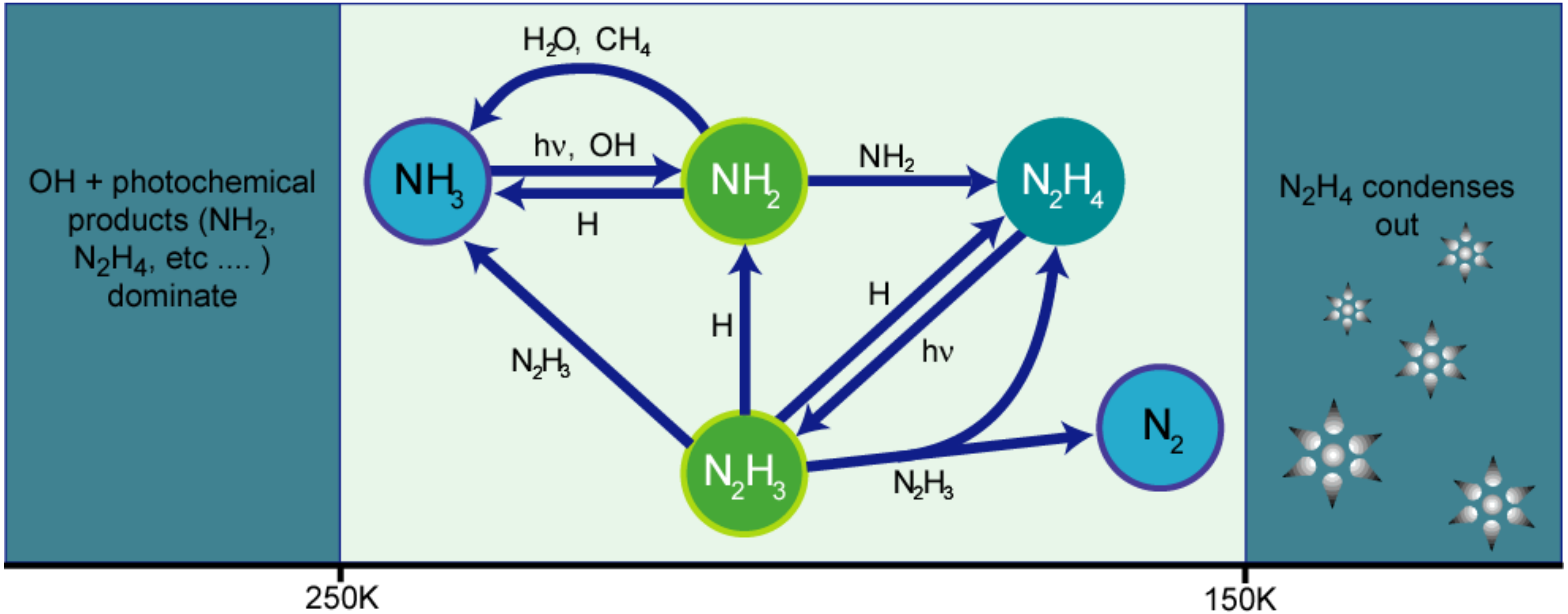
nitrogen formation

- delivered as N_2 trapped in ice - *no*:
  - very small ^{36}Ar, and no Xe, Kr detected



rare gas experiment averaged spectrum (with background subtracted) [Niemann et al., 2005]

N_2 from NH_3 on Primordial Titan



isotopes

$^{14}N/^{15}N_{Titan} << {}^{14}N/^{15}N_{Earth}$

nitrogen
escape

$^{12}C/^{13}C_{Titan} \sim {}^{12}C/^{13}C_{Earth}$

methane
replenishment

Why is methane important?

Role of methane in Titan's atmosphere

- provides warming, due to
  - hydrocarbon haze in stratosphere (~100 K), and
  - H_2-N_2 and CH_4-N_2 opacity in troposphere (~20 K)

- (warming) *critical* to sustain the very atmosphere
- of nitrogen,
  no CH_4 → little N_2 (condensation)

Fate of methane

- destroyed *irreversibly* by photochemistry in 10-30 million years

How to replenish methane?

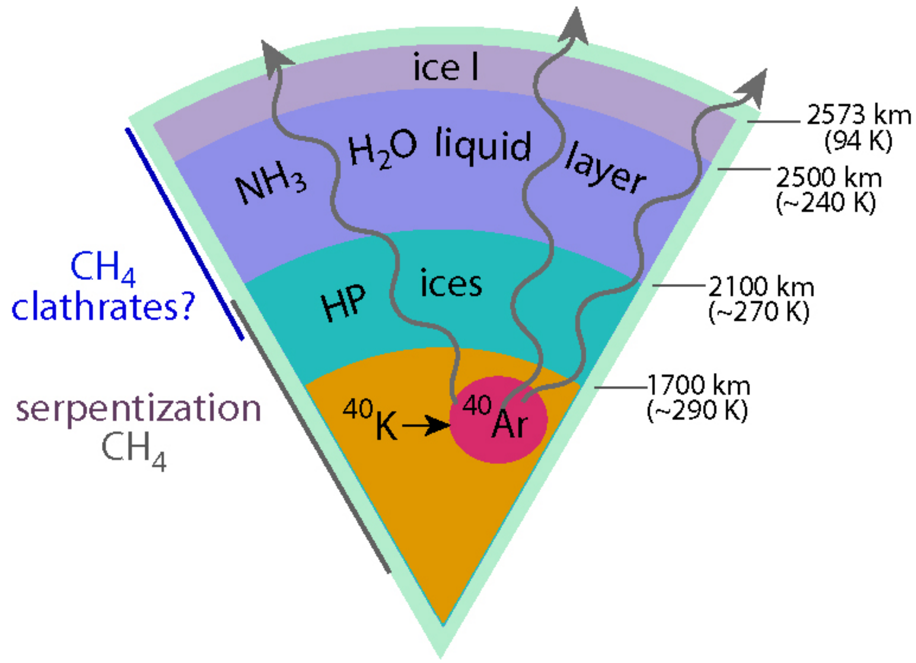
meteorology → no;

biology → no;

Outgassing from the interior (cryovolcanism)

- trapped in CH4 clathrates
- hydrogeochemically (serpentinization) → ?!

Cryovolcanism/outgassing



Grasset, Tobie et al.

What could be the potential sources of methane in Titan?

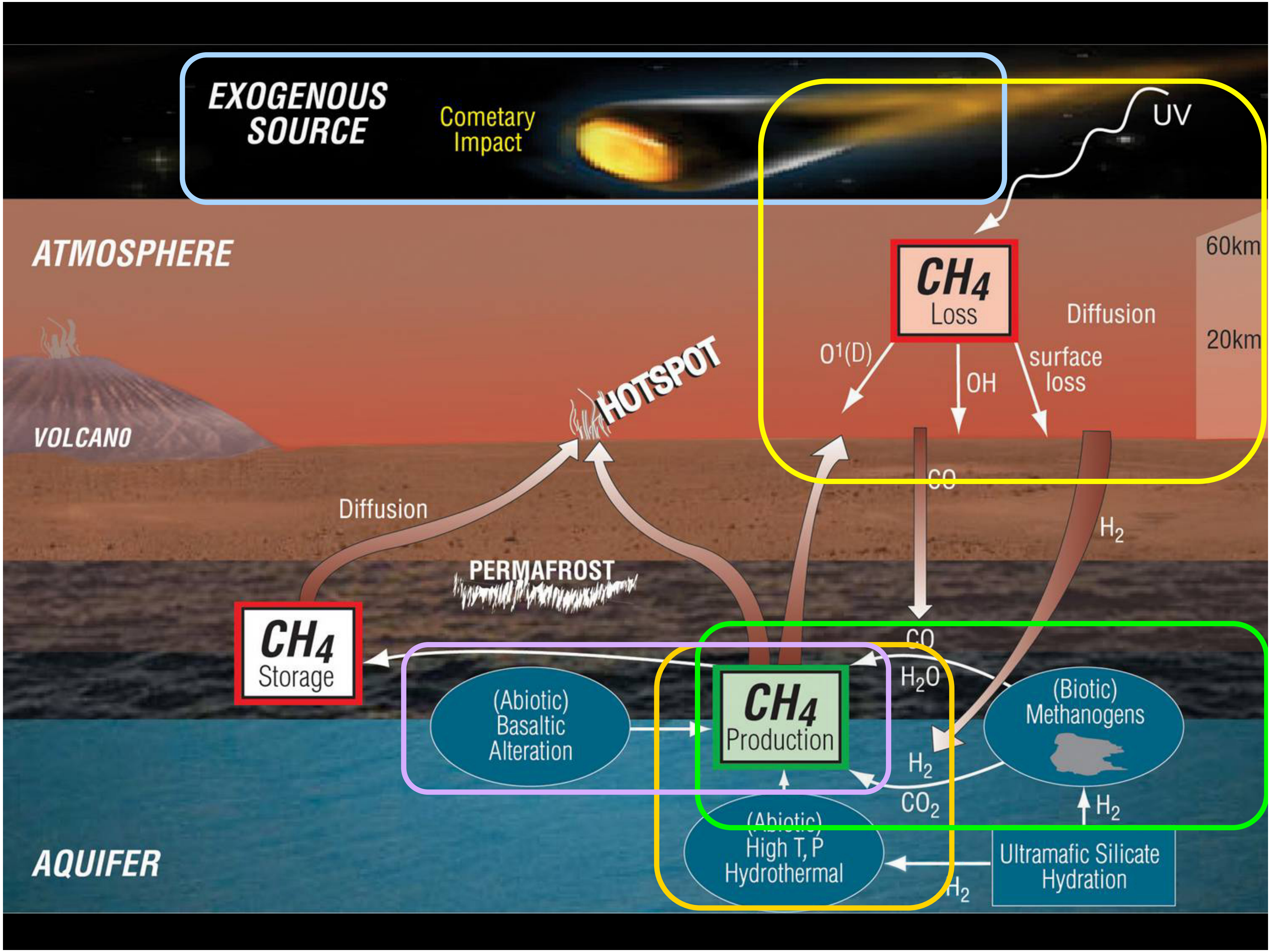
- ✓ Methane produced from the **gas phase conversion** of **CO** and **CO_2** in an **initially warm and dense Saturn's subnebula** (Prinn & Fegley 1981).

  Methane would have been trapped within Titan's building blocks during their formation in the cooling subnebula.

- ✓ Methane produced from **serpentinization reactions** (i.e. interaction between water and rock) in the interior of Titan (Atreya et al. 2006)

- ✓ Methane originating from the solar nebula, implying that **Titan's building blocks were formed from material originating from the primitive nebula** (Mousis et al. 2009)

However, any scenario describing a possible origin for the observed methane has to account for its present high D/H atmospheric ratio of 1.32 x 10^{-4} (Bézard et al., 2007, Coustenis et al., 2003, 2007), which represents an enrichment of about 4.5–7.2 times the protosolar value.


EXOGENOUS SOURCE
Cometary Impact
UV
ATMOSPHERE
60km
20km
CH4 Loss
Diffusion
O1(D)
OH
surface loss
VOLCANO
HOTSPOT
Diffusion
CO
H2
PERMAFROST
CH4 Storage
CO
H2O
(Abiotic) Basaltic Alteration
CH4 Production
(Biotic) Methanogens
H2
CO2
H2
(Abiotic) High T, P Hydrothermal
Ultramafic Silicate Hydration
H2
AQUIFER

Production of methane from serpentinization reactions in the interior of Titan

In terrestrial oceans, hydrothermal fluids and seawater interact with peridotite via the following summary reaction (Moody 1976; Atreya et al. 2006):

Peridotite (olivine/pyroxene) + water ➔ serpentine + brucite + magnetite + hydrogen.

CH_4 can be formed in the interior of Titan from the association of CO_2 or carbon grains with the H_2 formed during the hydrothermal alteration of peridotite.

If serpentinization in the interior of Titan is at the origin of the atmospheric methane, then the observed D/H value must be consistent with this mechanism.

Computation of the D/H fractionation associated with serpentinization depends on the size of the rock and liquid water reservoirs and on the original D/H ratio in water.

Methane Origin

1. methanogens - *no*: ^{13}C deficiency not seen

- Earth
  - biogenic $^{12}C/^{13}C$ 92- 96 (organic)
  - inorganic $^{12}C/^{13}C$ 89.4 (V-PDB inorganic std.)

    (similar to Saturn, Jupiter, Sun)
- Titan $^{12}C/^{13}C$ 82.3±1

2. arrived as clathrate - *possible*:

   but no Xe, Kr, and very low ^{36}Ar detected

3. produced on Titan → hydrothermal source - *possible*

   but temperature, pressure problem …

Characteristics of Titan

- ✓ Atmosphere dominated by N_2 and CH_4
  $CO/CH_4 << 1$ --> **What happened to CO?**

- ✓ N_2 would result from the NH_3 photolysis or shock chemistry (Atreya et al. 1978; McKay et al. 1988). **So, N_2 is probably not primordial!!**

- ✓ High CH_3D/CH_4 ratio (Orton 1992; Coustenis et al., 2007; Bézard et al. 2007): **atmospheric methane probably formed in the solar nebula and NOT via hydrothermal reactions in the interior of Titan** (Mousis et al. 2009c) **or via gas phase chemistry in Saturn's subnebula** (Mousis et al. 2002)

- ✓ **Deficiency of Titan's atmosphere in primordial noble gases**. Only low amounts of ^{36}Ar have been detected (Niemann et al. 2005)

- ✓ **D/H ratio found to be cometary in Enceladus:** the building blocks of Titan and Enceladus were formed in the nebula (Waite et al. 2009).

Formation of Titan: summary

Conditions required to explain the current composition of Titan's atmosphere:

- **Volatiles were trapped in Saturn's feeding zone in the form of hydrates, clathrates or pure condensates**

- **Partial vaporization of solids accreted by Titan at about 50 K in Saturn's subnebula: loss of CO and Ar; preservation of primordial CH_4, NH_3, CO_2, Kr and Xe**

Two possibilities to explain the deficiency of Xe and Kr in Titan:

- **Efficient trapping of Xe and Kr in clathrates formed on the surface of Titan**

- **Formation of Xe-H_3^+ and Kr-H_3^+ complexes in the solar nebula that impede the condensation of Xe and Kr or their incorporation in the forming clathrates**

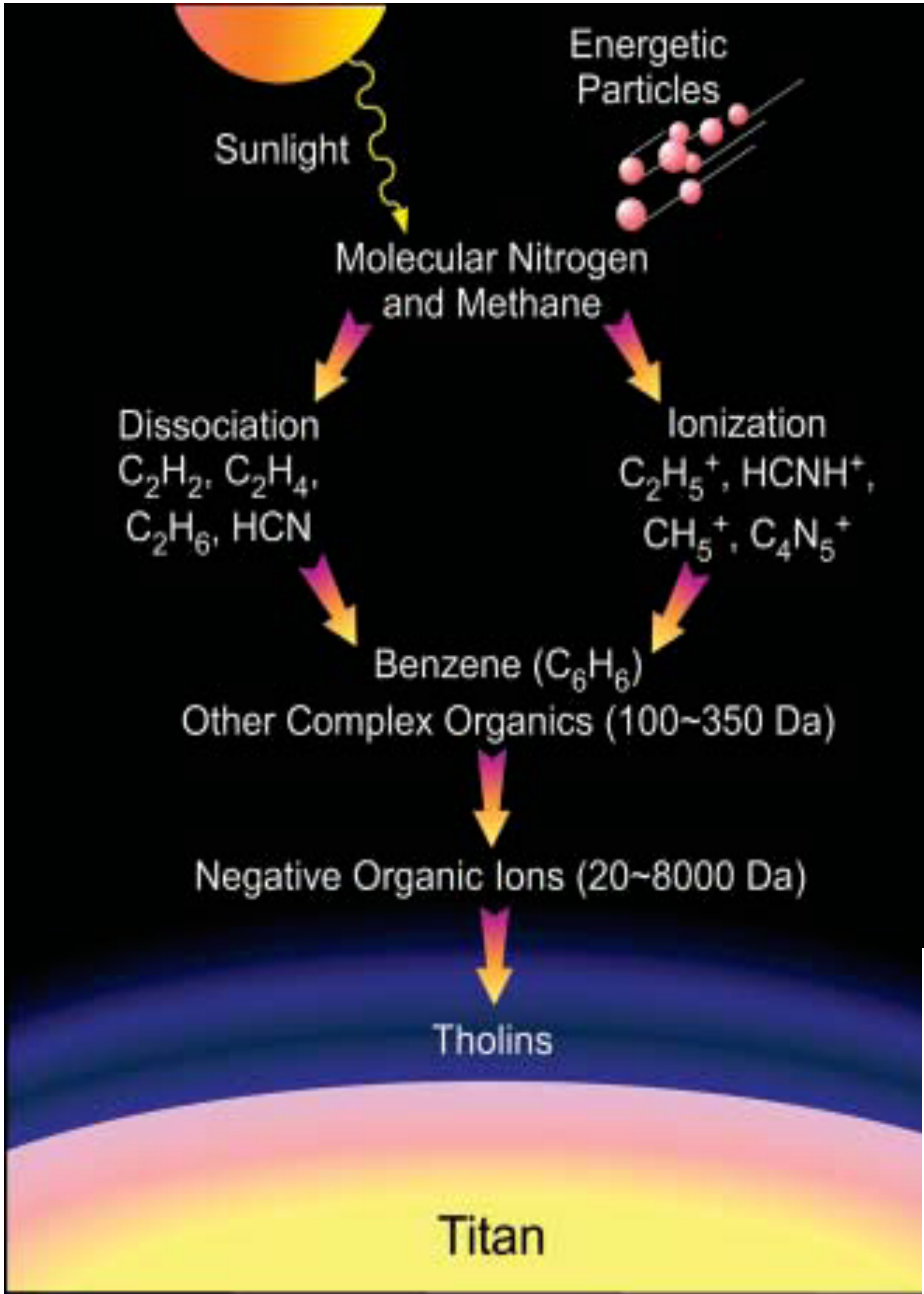
Conclusions

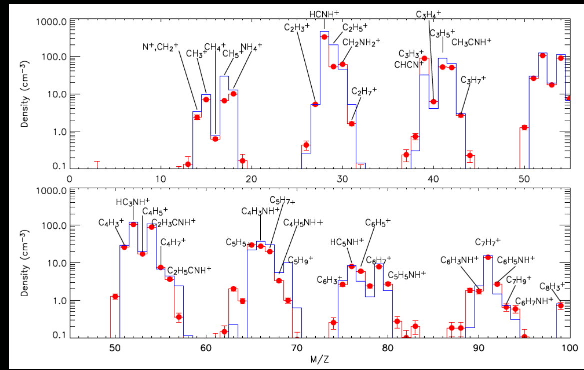
- Nitrogen and methane were *not* delivered to Titan;
  however, ammonia and carbon (grains, organics, CO, CO_2) were.

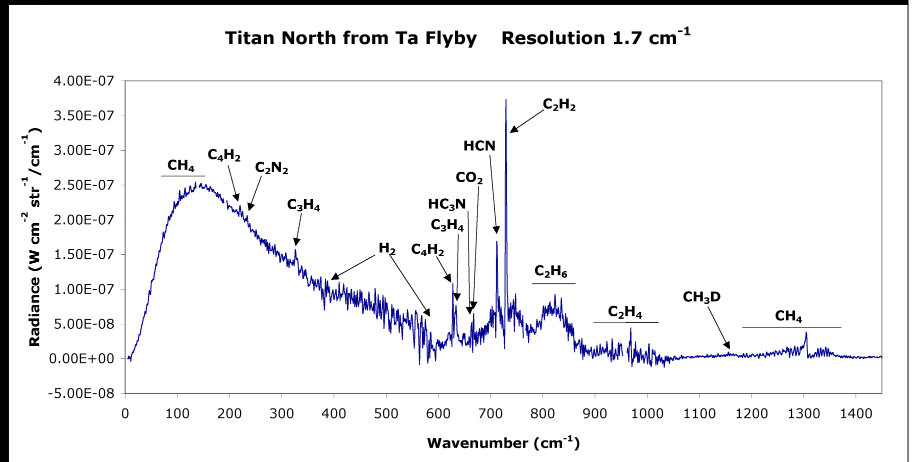
- N_2 and CH_4 are produced *on* Titan
  N_2 from NH_3 photochemistry
  CH_4 from hydrogeochemistry or CH_4 clathrates

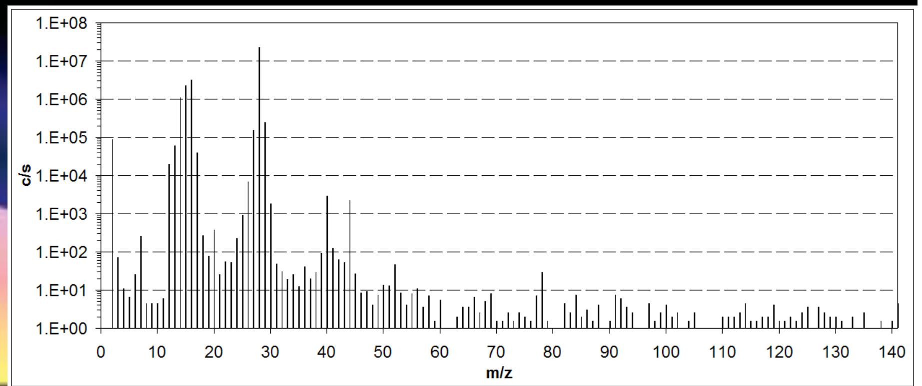
Life *as we know it* is not responsible for Titan's methane.

Evolution of Titan's atmospheric composition

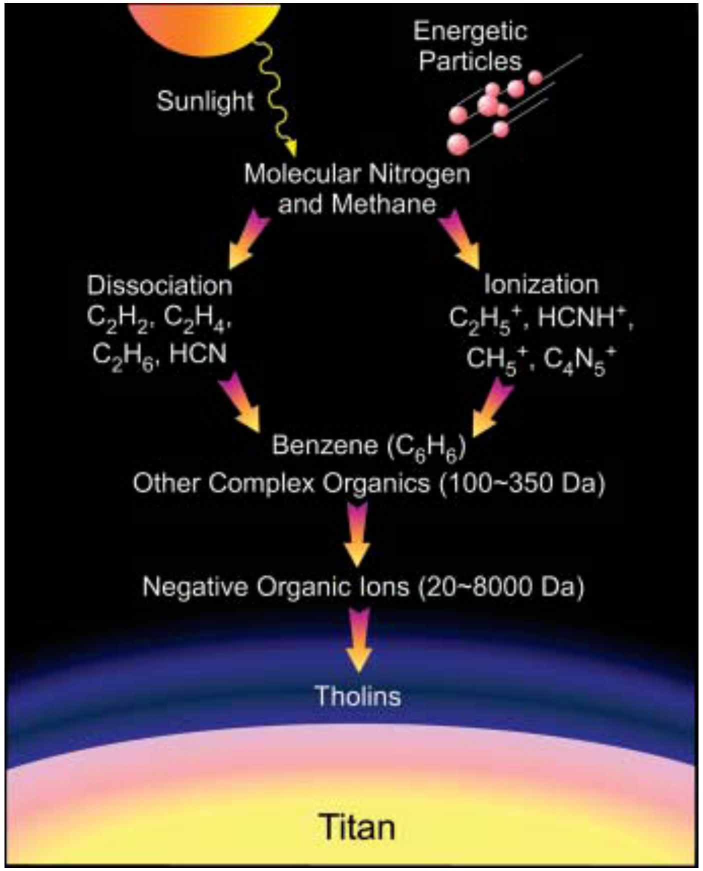

Sunlight
Energetic Particles
Molecular Nitrogen and Methane
Dissociation
C_2H_2, C_2H_4, C_2H_6, HCN
Ionization
$C_2H_5^+$, $HCNH^+$, CH_5^+, $C_4N_5^+$
Benzene (C_6H_6)
Other Complex Organics (100~350 Da)
Negative Organic Ions (20~8000 Da)
Tholins
Titan


Density (cm⁻³)
M/Z

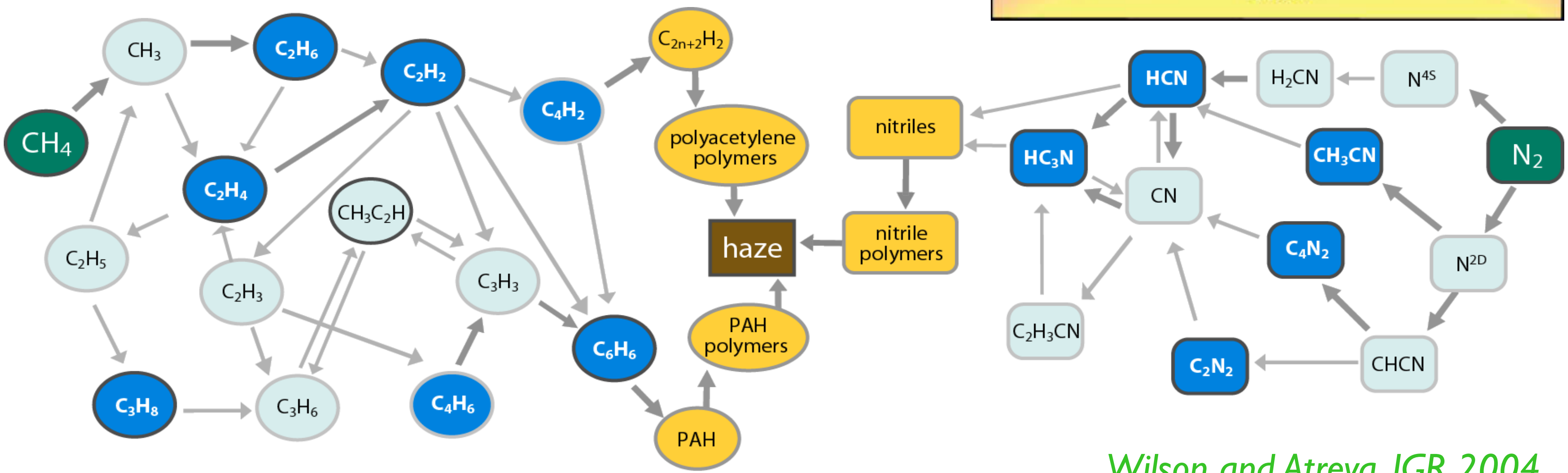

Titan North from Ta Flyby Resolution 1.7 cm⁻¹
Radiance (W cm⁻² str⁻¹/cm⁻¹)
Wavenumber (cm⁻¹)
CH4
C4H2
C2N2
C3H4
H2
C4H2
HC3N
C3H4
CO2
HCN
C2H2
C2H6
C2H4
CH3D
CH4


c/s
m/z

Organic chemistry on Titan



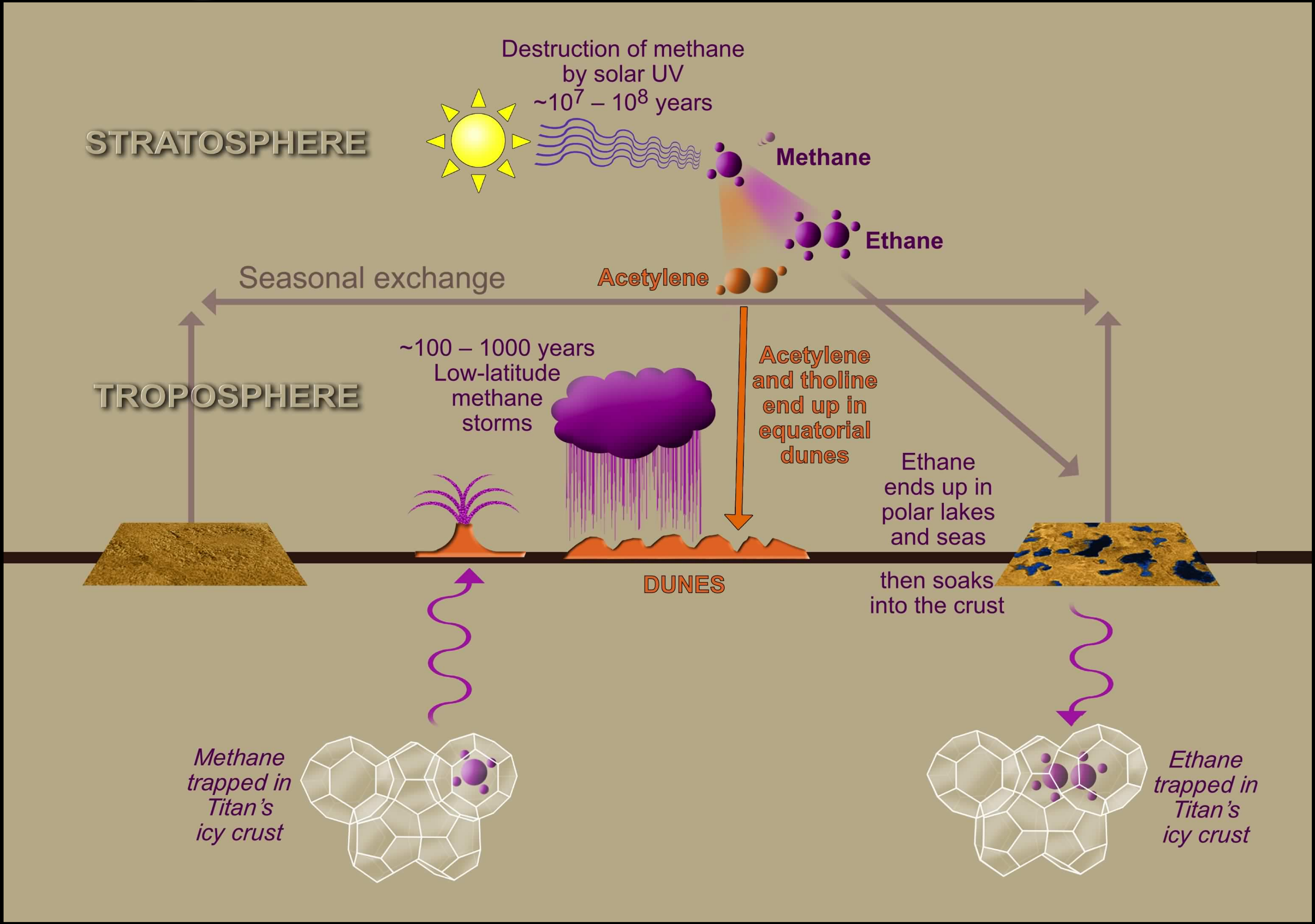
Cassini/INMS on Titan: Waite et al (2006)



Wilson and Atreya, JGR 2004

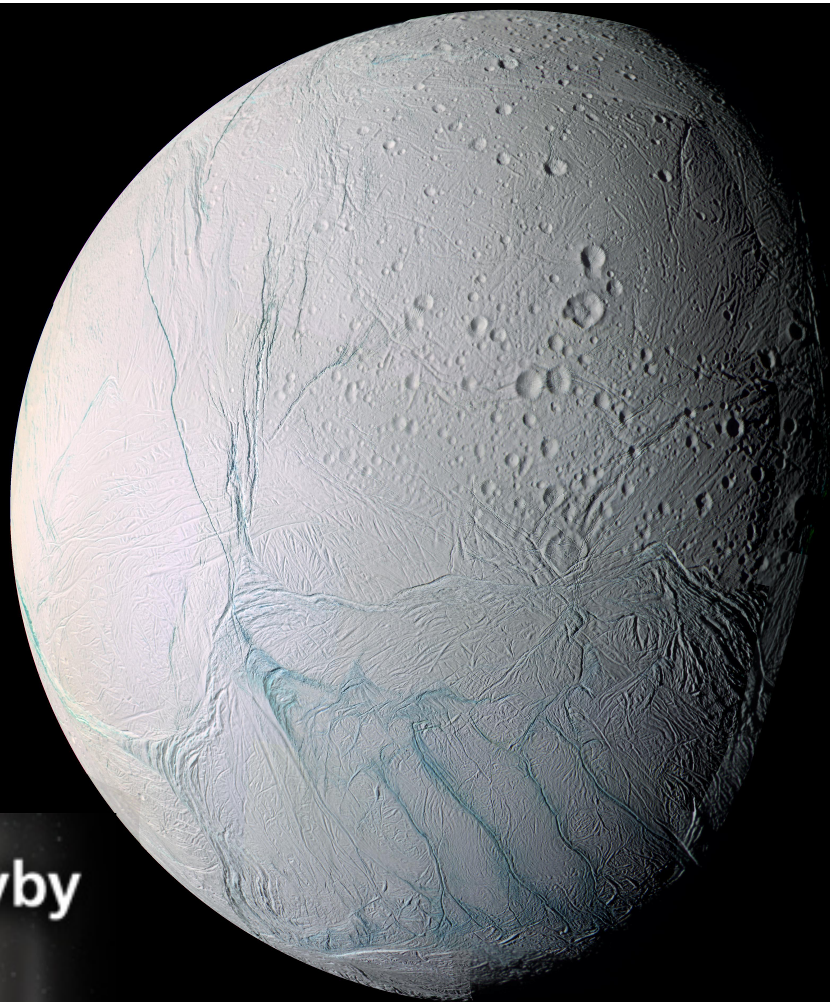
Fate of Titan

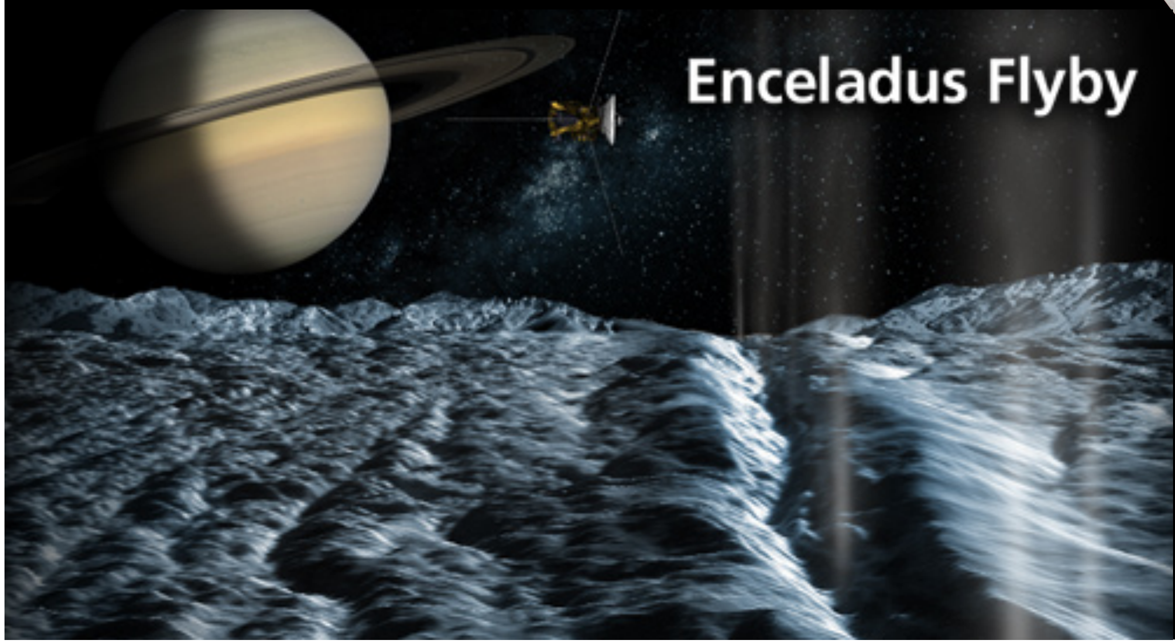
Titan's methane cycle: a volatile in flight, Earth's future climate?



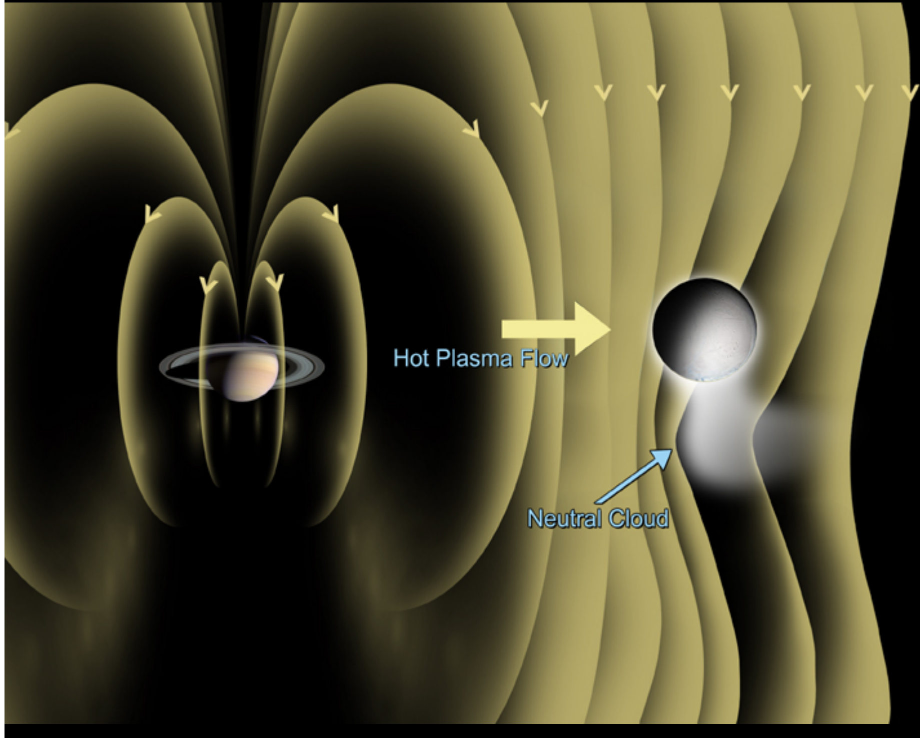
Enceladus

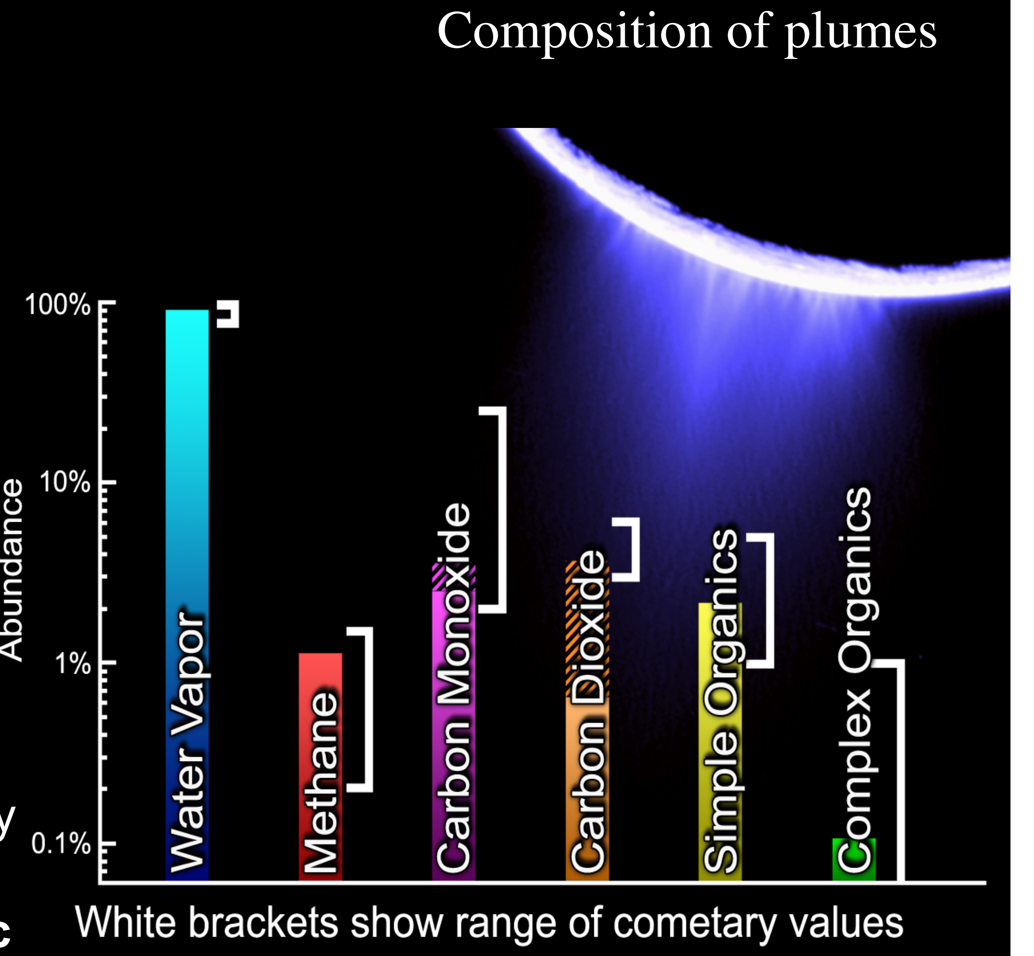
And the « tiger stripes »





Enceladus plumes

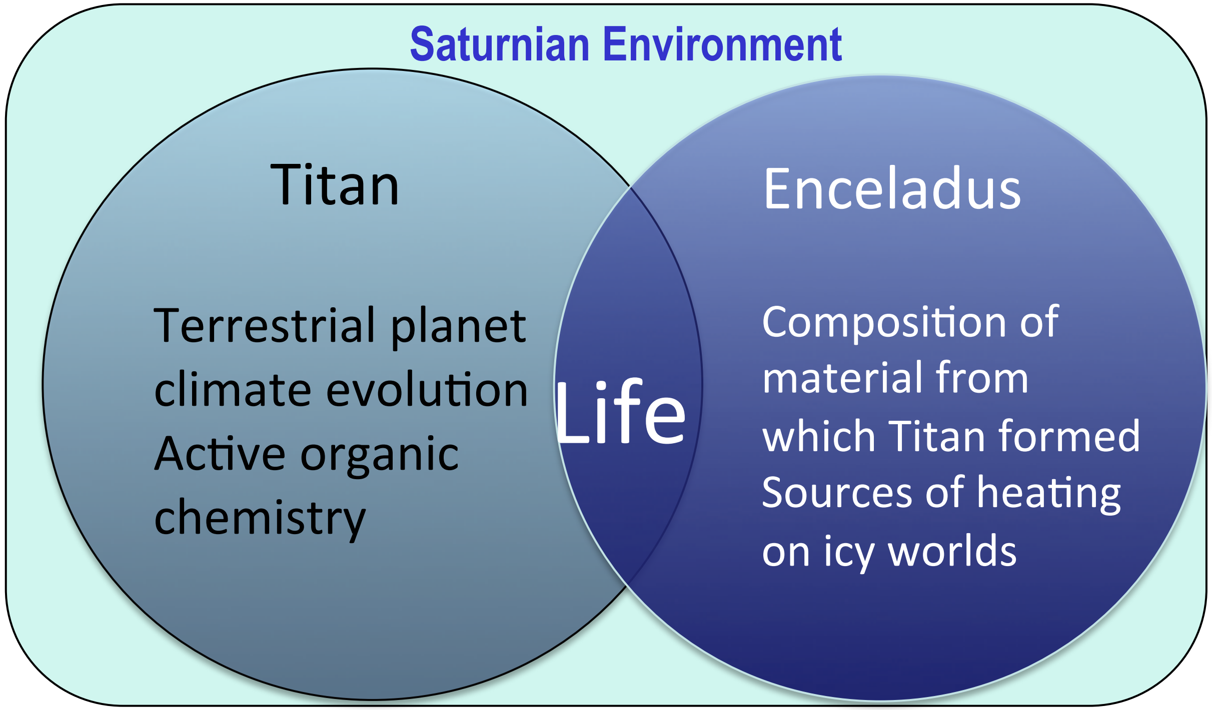




- What is the origin of the plumes

- **Water vapor ejecta far away from the Sun** (strong implications for the habitability zones)
- **Indications for the presence of organic chemistry**

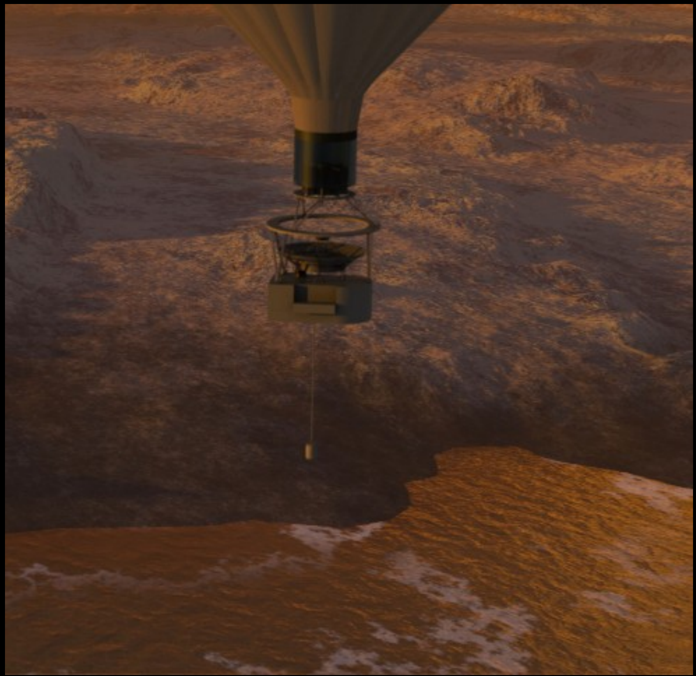
Moons in the Saturnian system



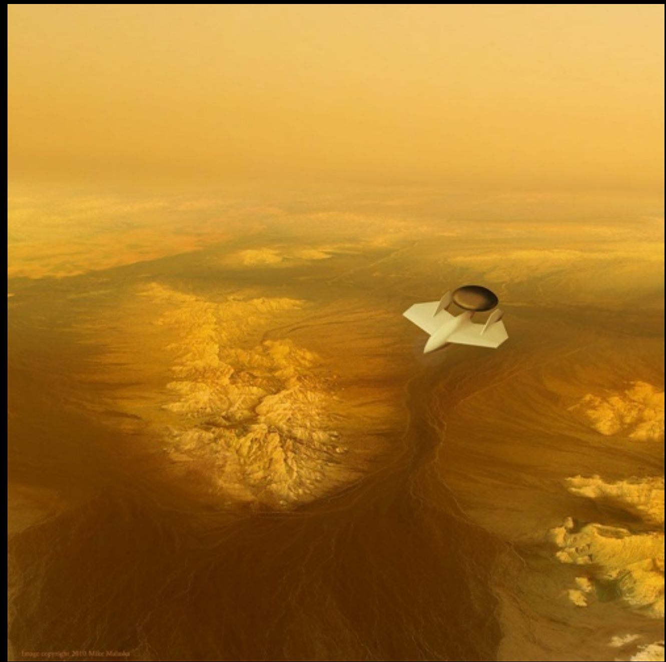
–The Saturnian system is rich in worlds that could bring insights on important aspects of Earth's

- *climate,*
- *organic chemistry and*
- *emergence of life*.

Ideas/studies for returning to Titan



TSSM: Balloon, lander & orbiter



AVIATR /PLANE

TIME: Lake lander