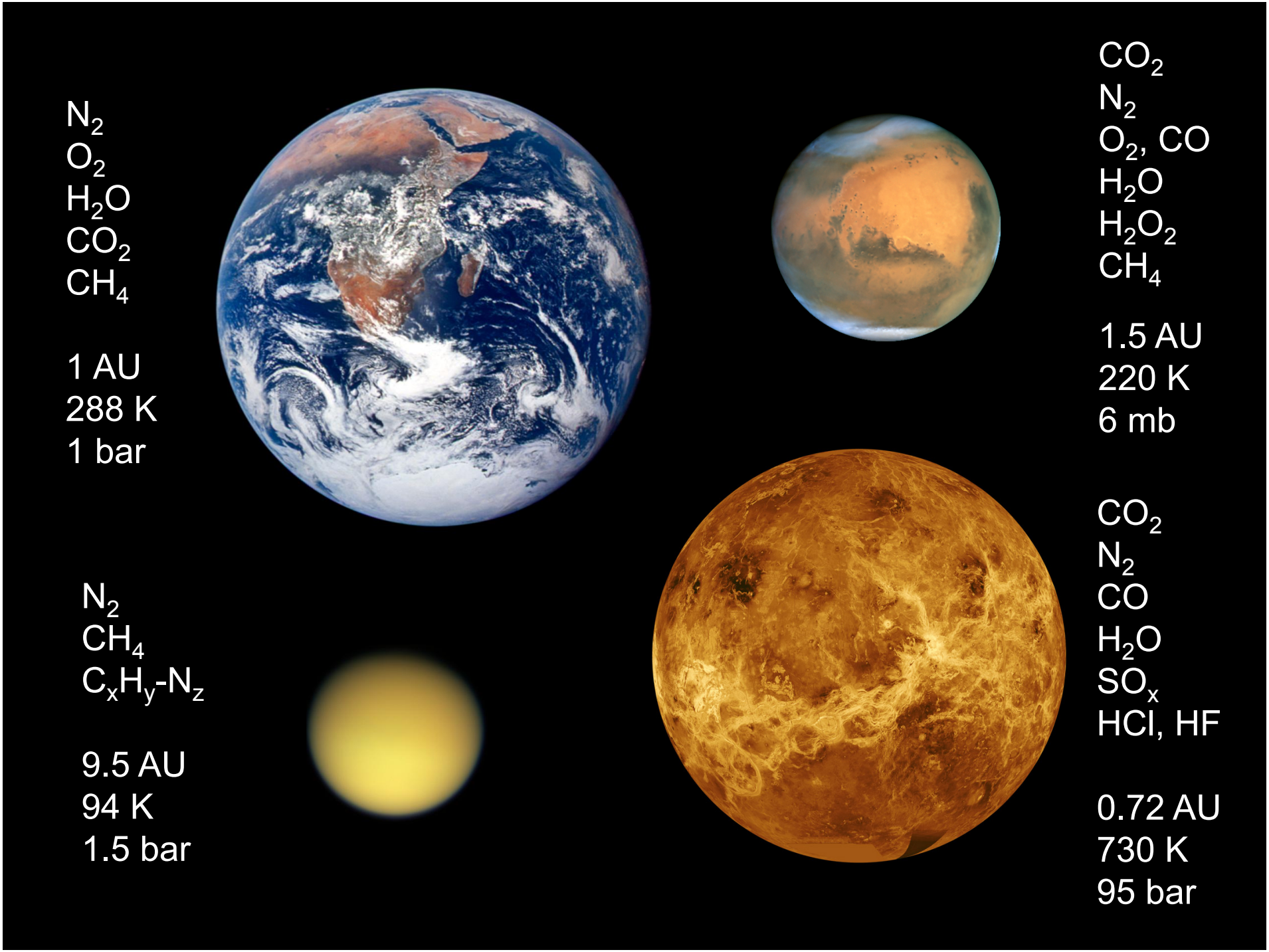
The Origin, Evolution, and Cycle of Titan's Nitrogen-Methane Atmosphere

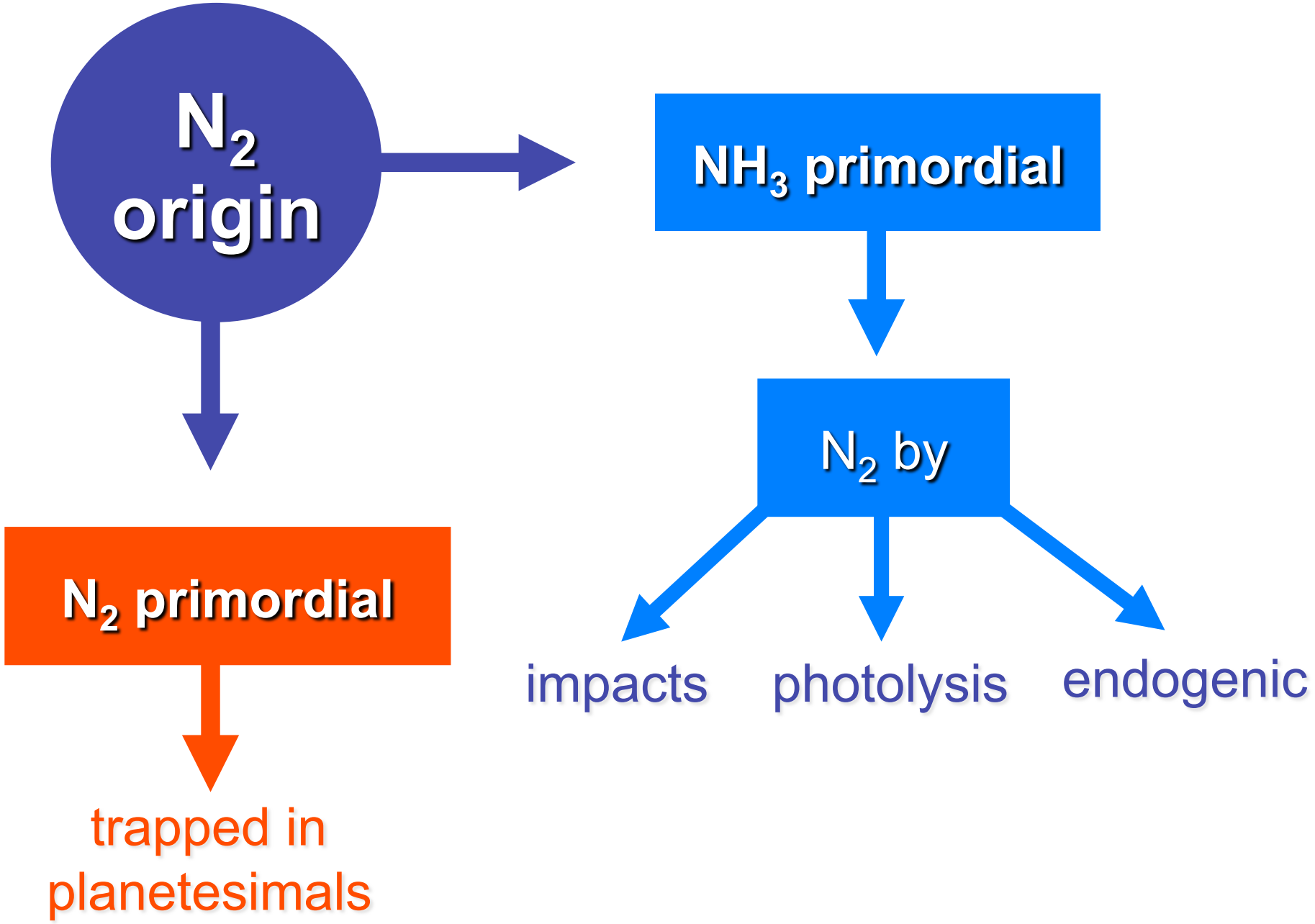
sushil atreya

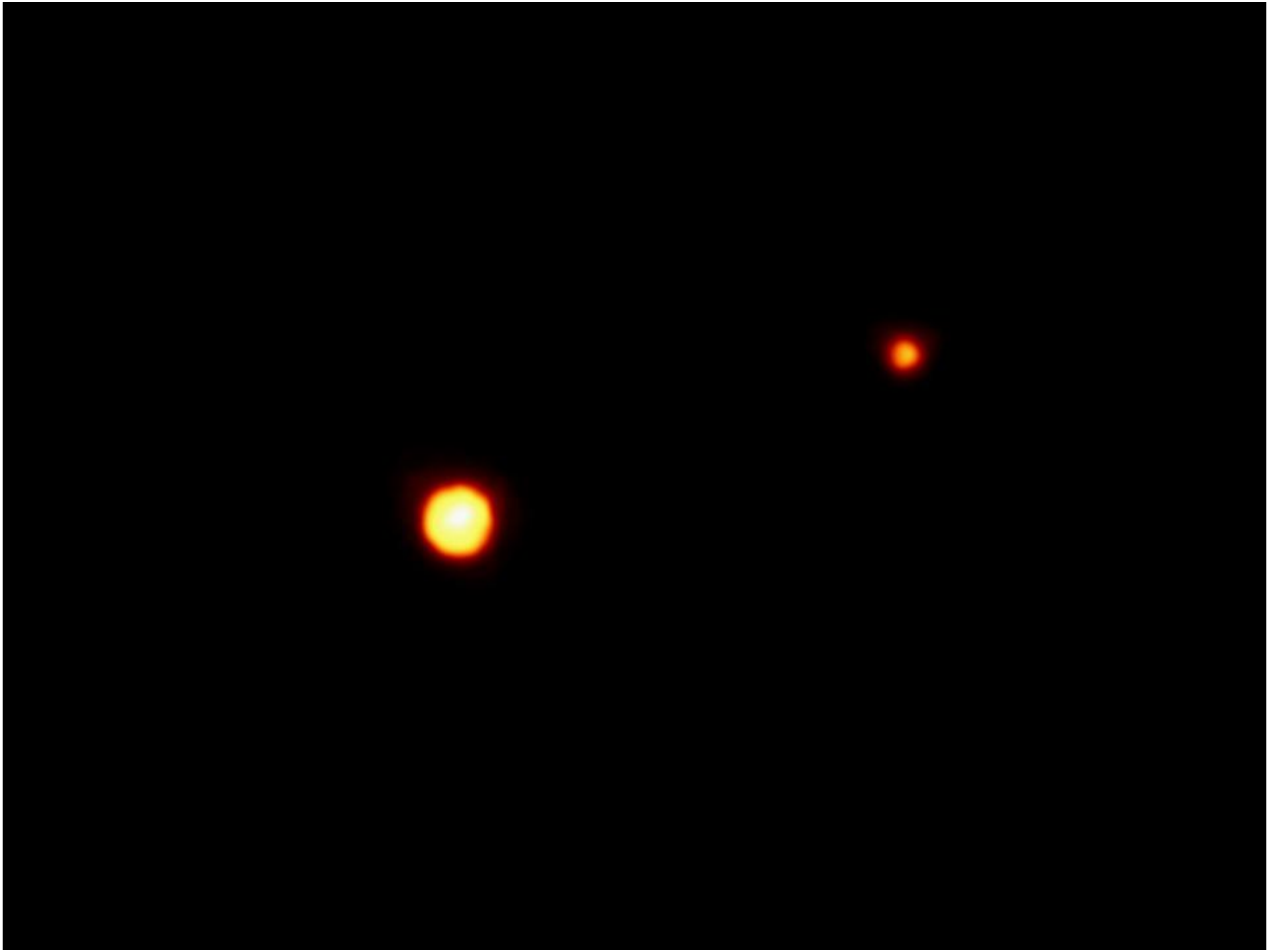
Exoclimes Exeter 2010

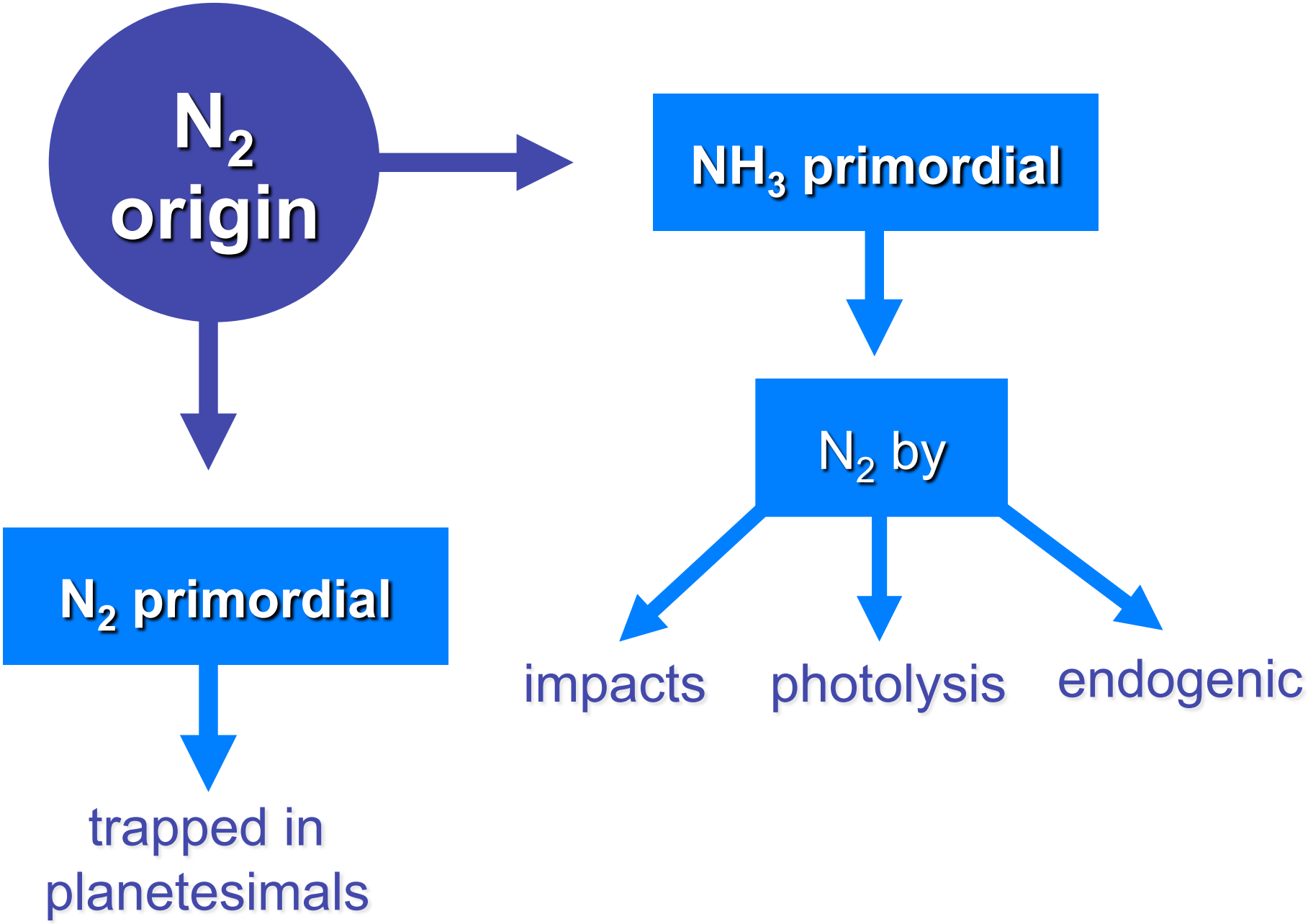

N_2
O_2
H_2O
CO_2
CH_4
1 AU
288 K
1 bar
CO_2
N_2
O_2, CO
H_2O
H_2O_2
CH_4
1.5 AU
220 K
6 mb
N_2
CH_4
C_xH_y-N_z
9.5 AU
94 K
1.5 bar
CO_2
N_2
CO
H_2O
SO_x
HCl, HF
0.72 AU
730 K
95 bar

map

- Titan in Solar System Context
- Nitrogen Origin
- Methane Origin, Source
- Methane Cycle
- Prebiotic Molecules?
- Future?


N_2 origin
NH_3 primordial
N_2 by
impacts
photolysis
endogenic
N_2 primordial
trapped in planetesimals

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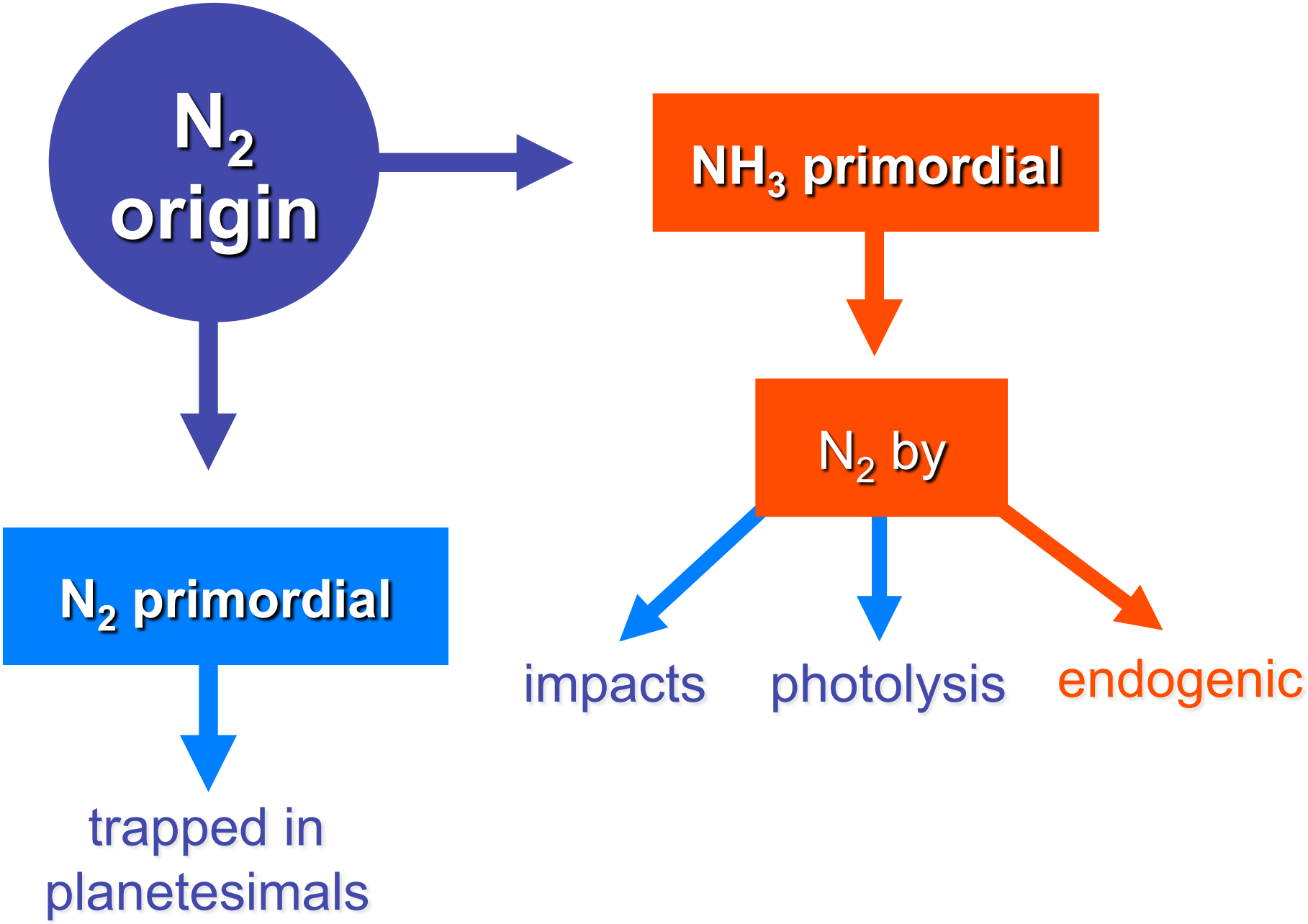
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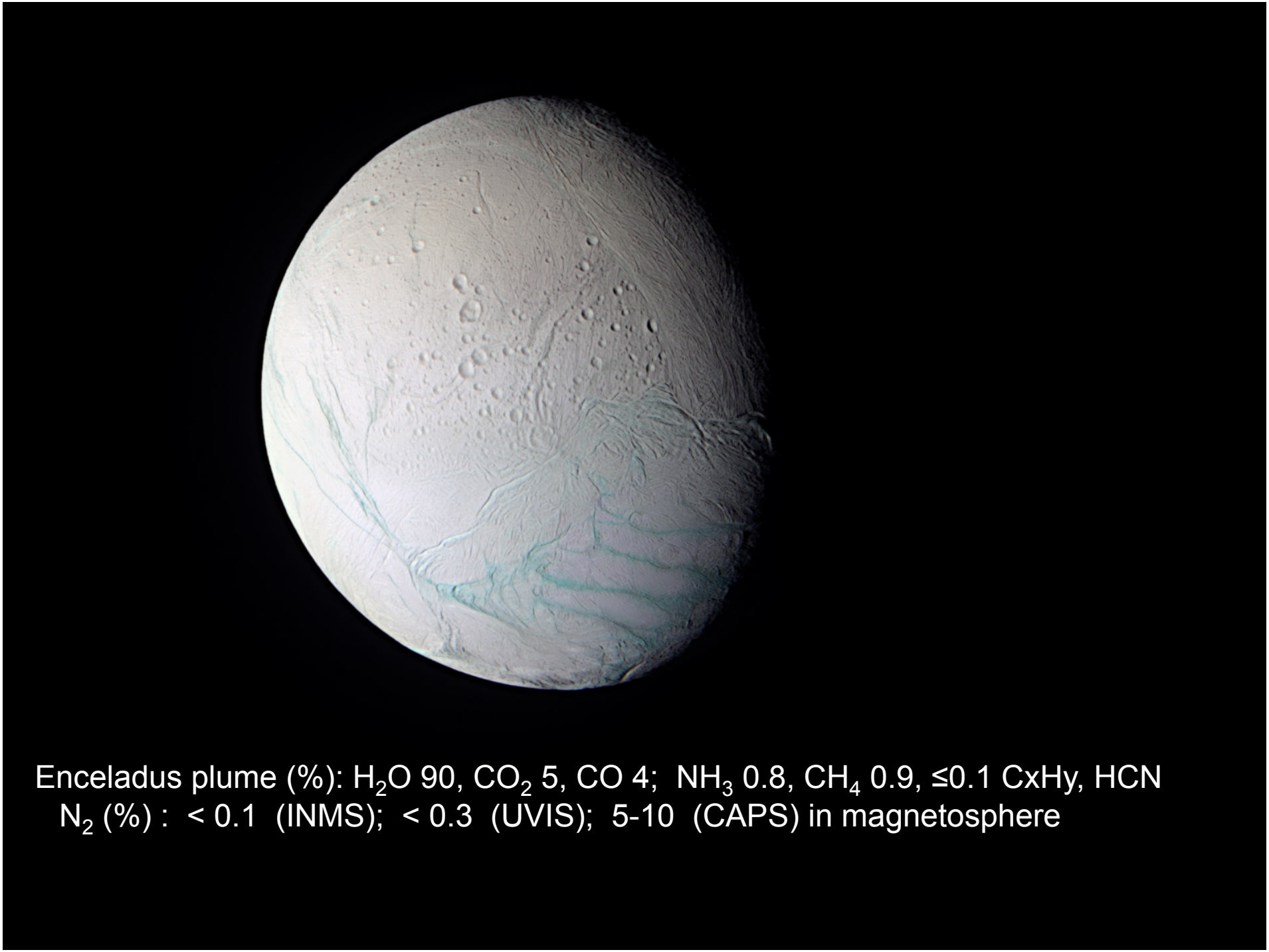


Enceladus plume (%): H_2O 90, CO_2 5, CO 4; NH_3 0.8, CH_4 0.9, ≤0.1 CxHy, HCN

N_2 (%) : < 0.1 (INMS); < 0.3 (UVIS); 5-10 (CAPS) in magnetosphere

N_2 by thermal decomposition of NH_3

- High temperatures (575 - 850 K):

  $2NH_3 \Leftrightarrow N_2 + 3H_2$

  q (N_2) = 0.7 at 35 MPa, 800 K

- Lower temperatures (<575 K):

  $2NH_3(aq) \Leftrightarrow N_2(aq) + 3H_2(aq)$

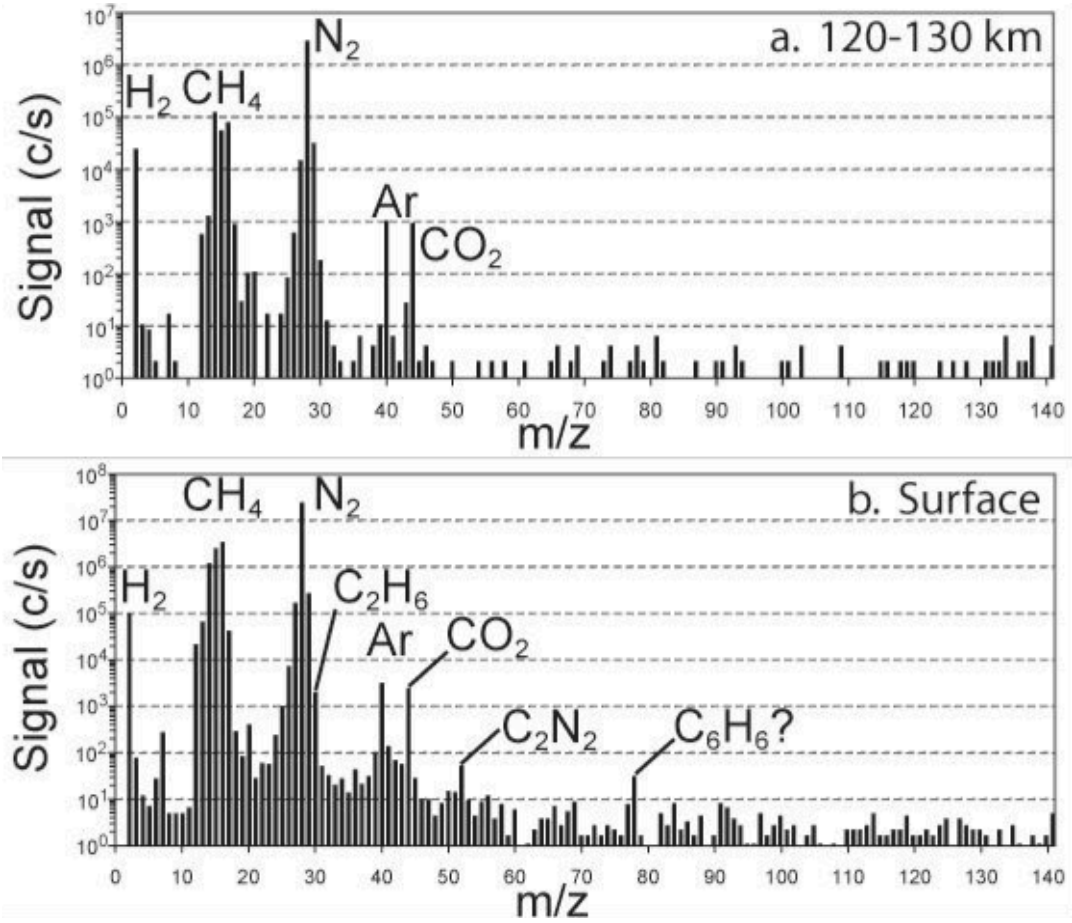
  - requires metal or clay mineral catalysis
  - reverse rxn inhibited due to reactant dispersal

  (Matson et al., 2007 Icarus)

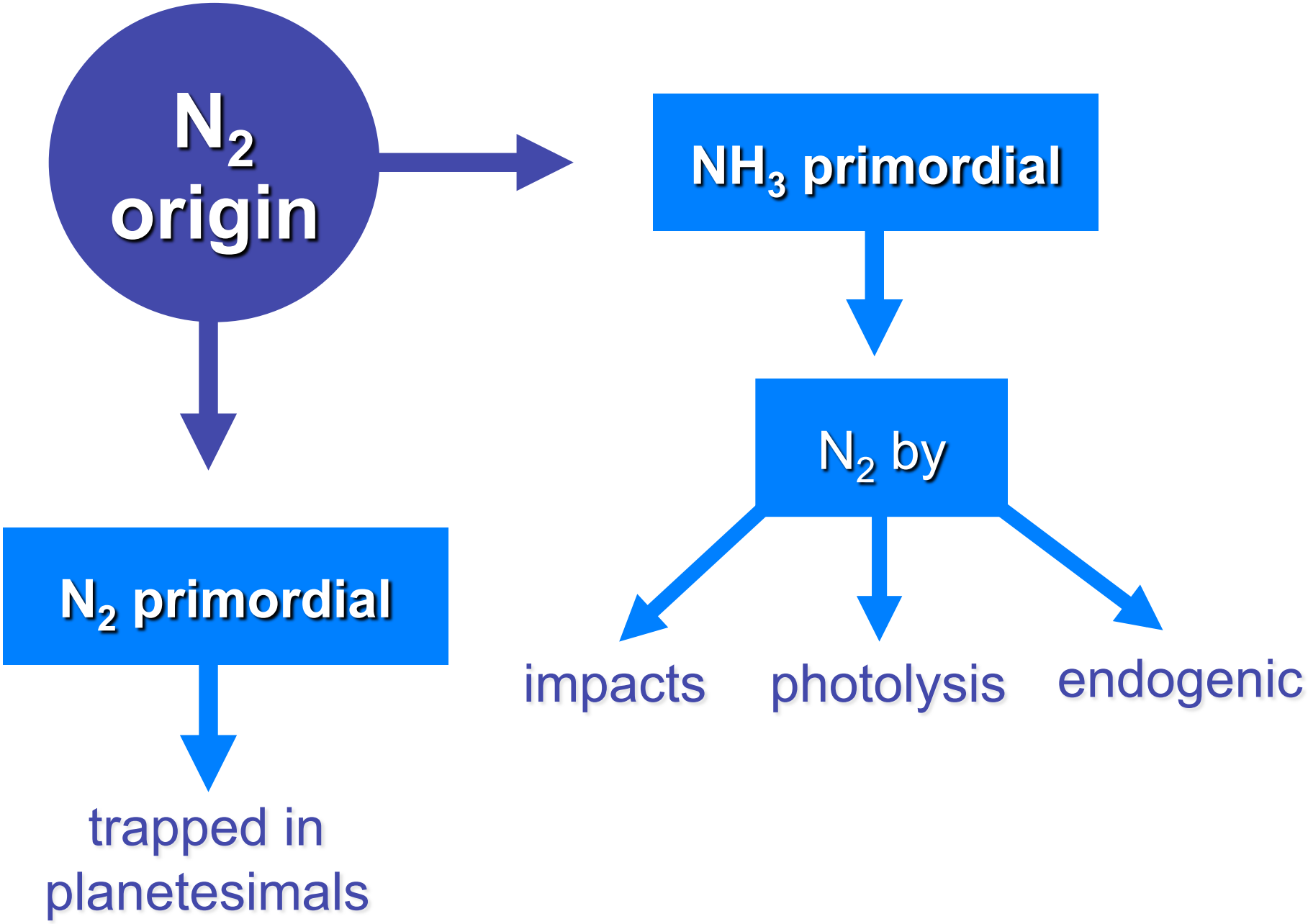
  Organic molecules produced by similar hydrothermal rxns (Foustouskos & Seyfried, 2004), and detected.

Huygens GCMS spectra of Titan

$^{36}Ar/N_2 = 2.1x10^{-7}$ *solar = 0.11*



(Niemann et al. 2005, 2010)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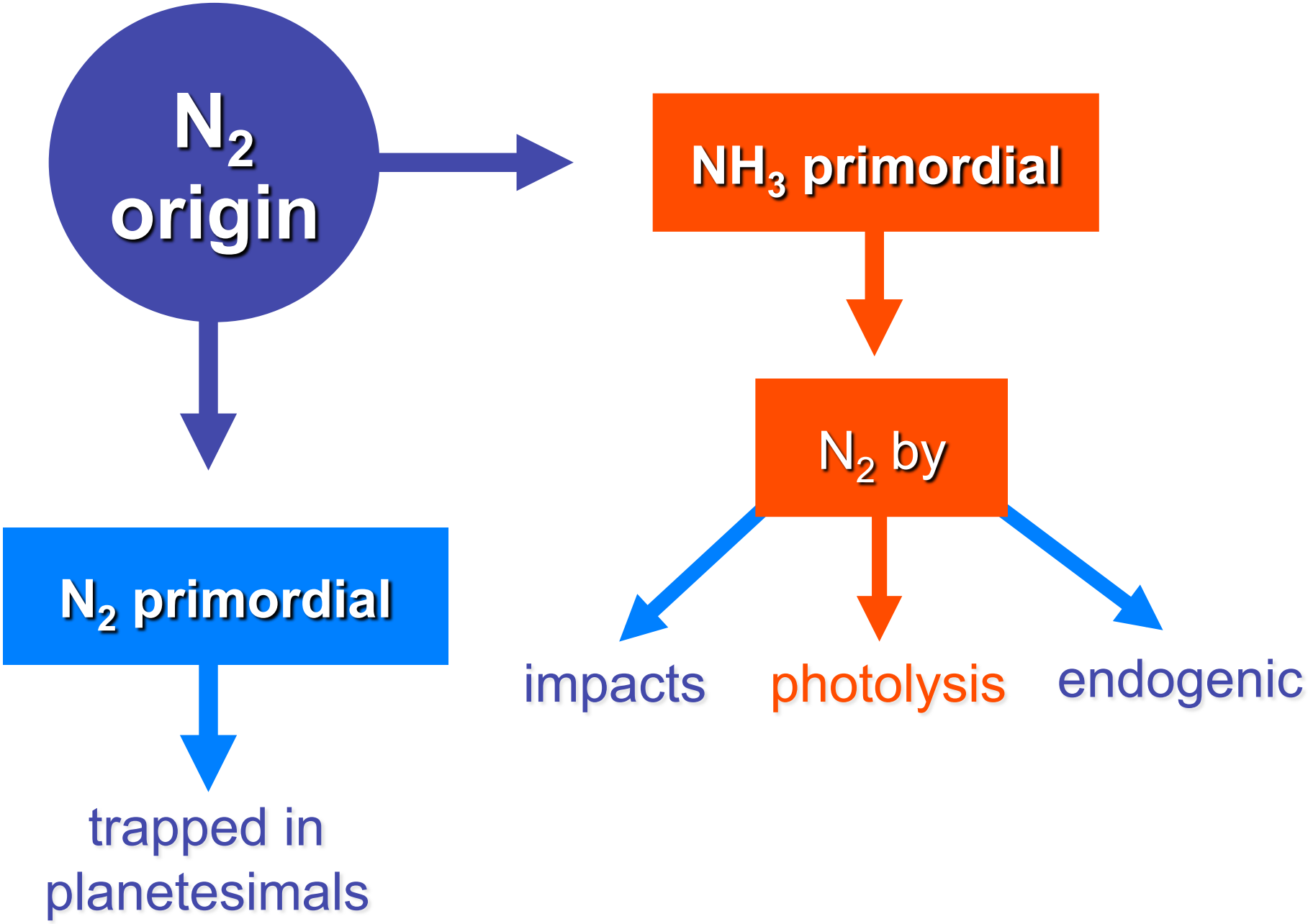
N_2 origin
NH_3 primordial
N_2 by
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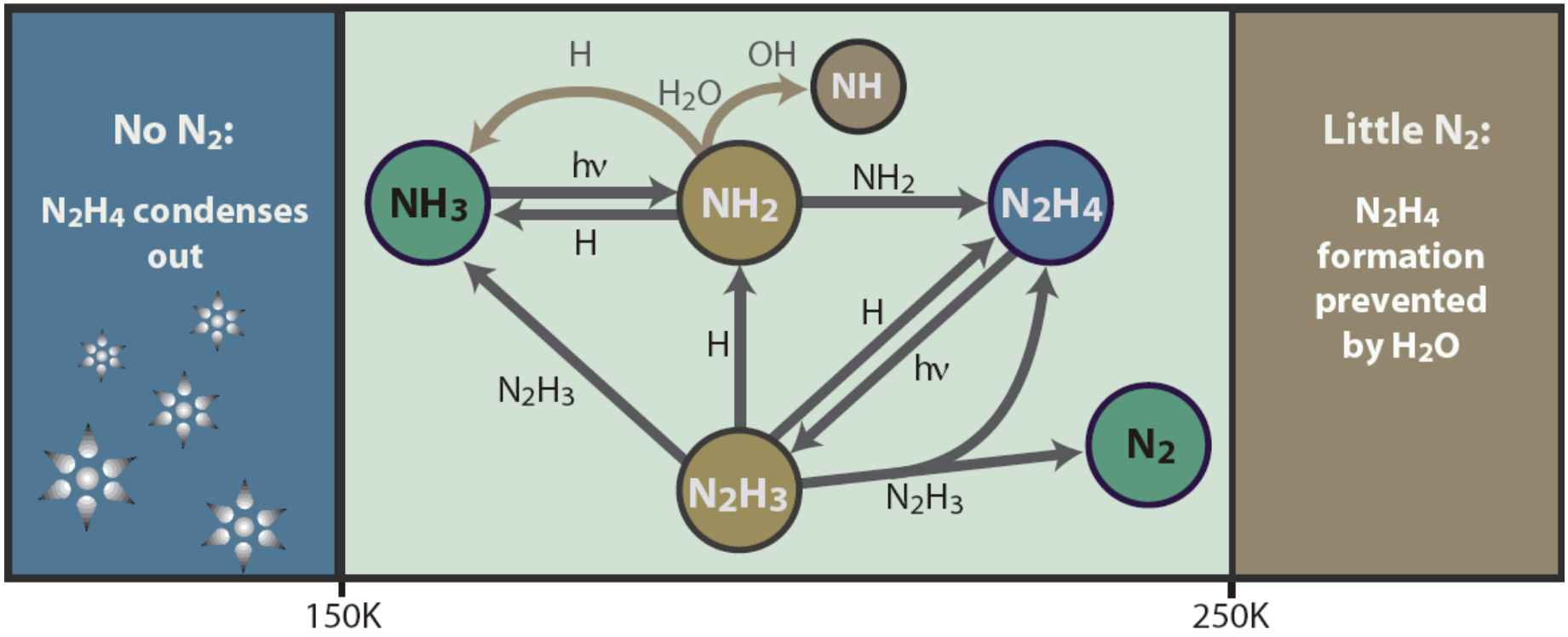
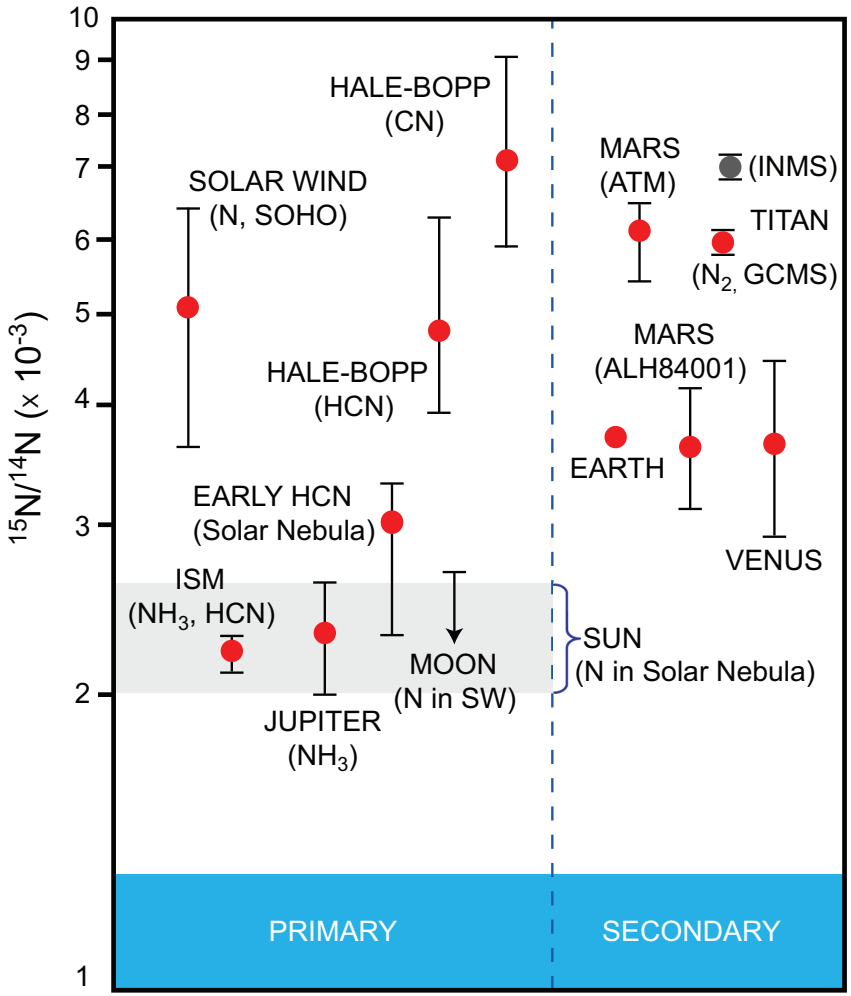
N_2 from NH_3 on primordial Titan
10 bars in 20-30 Myr



(Atreya et al. 1978; Atreya 1986; Adams and Atreya 2006; Adams 2006)

Titan's nitrogen isotopes similar to Earth's (& other terrestrial planets) or comets?



nitrogen and *methane* intertwined

On Titan, methane means "greenhouse" :

~100 K increase in stratosphere, due to hydrocarbon haze

~20 K increase in troposphere, due to CH_4-N_2, H_2-N_2, N_2-N_2 collision-induced opacity

Greenhouse (warming) critical to Titan's N_2 :

no CH_4 → little to no N_2 ;
N_2 condenses and atmosphere collapses!

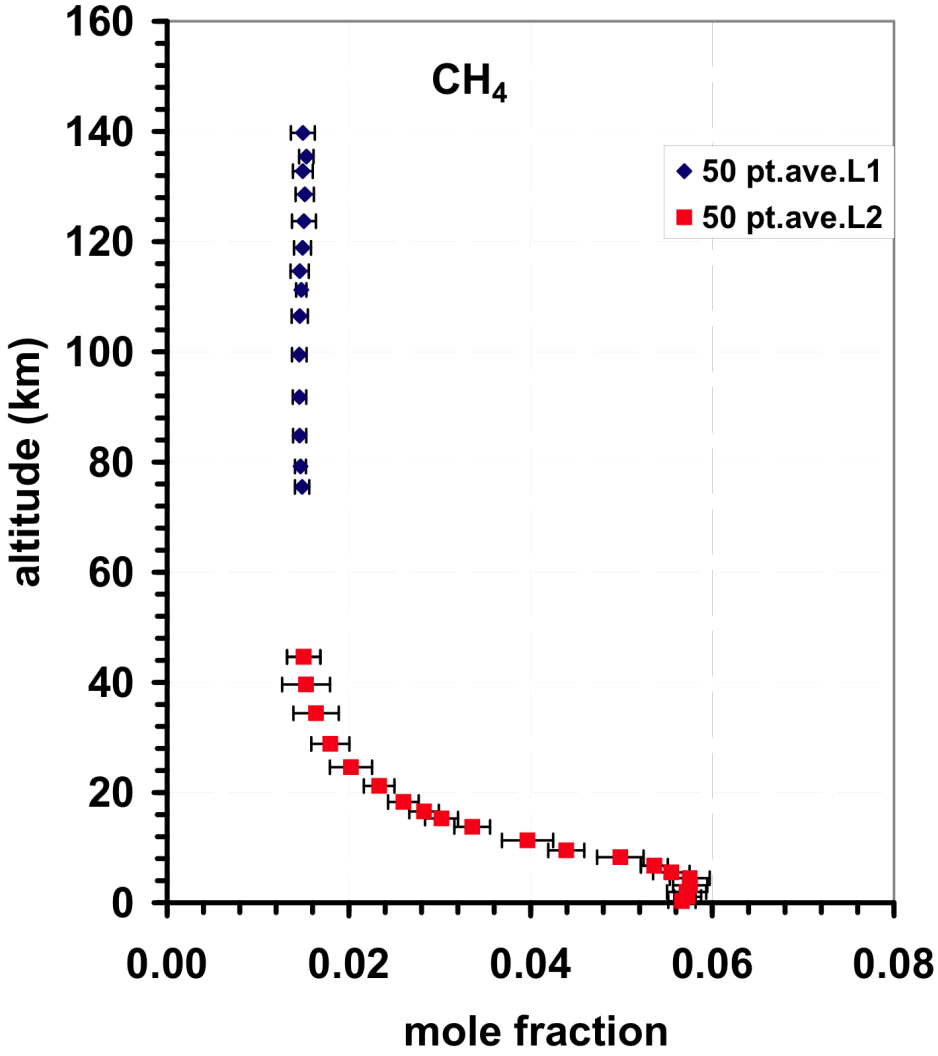
Origin of Titan's Methane :

Secondary, i.e. formed *on* Titan hydrogeochemically, or

Primordial, i.e. delivered *to* Titan directly as CH_4, or

Biological, i.e. produced by methanogens

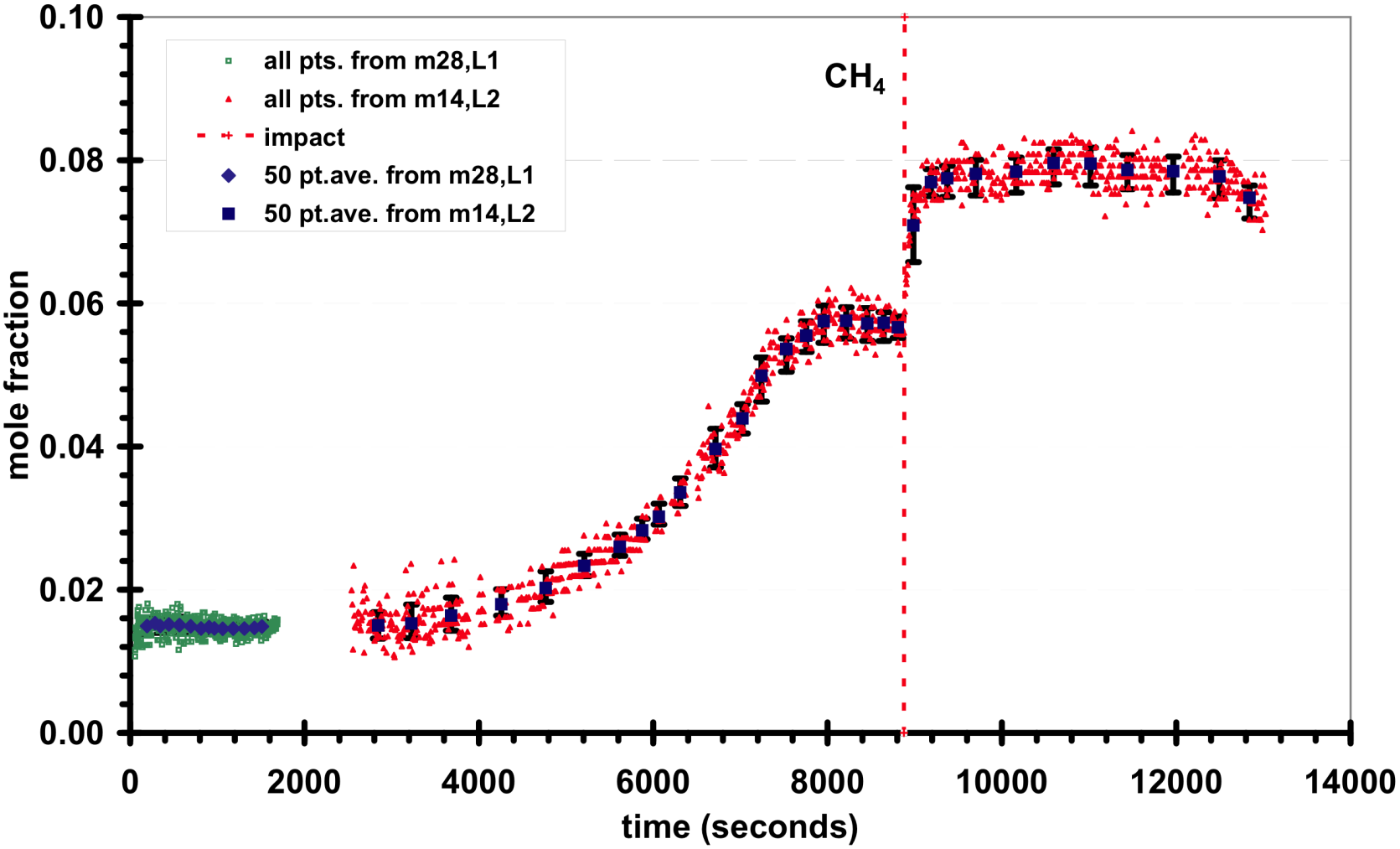
Huygens GCMS measures methane in troposphere, *in situ*



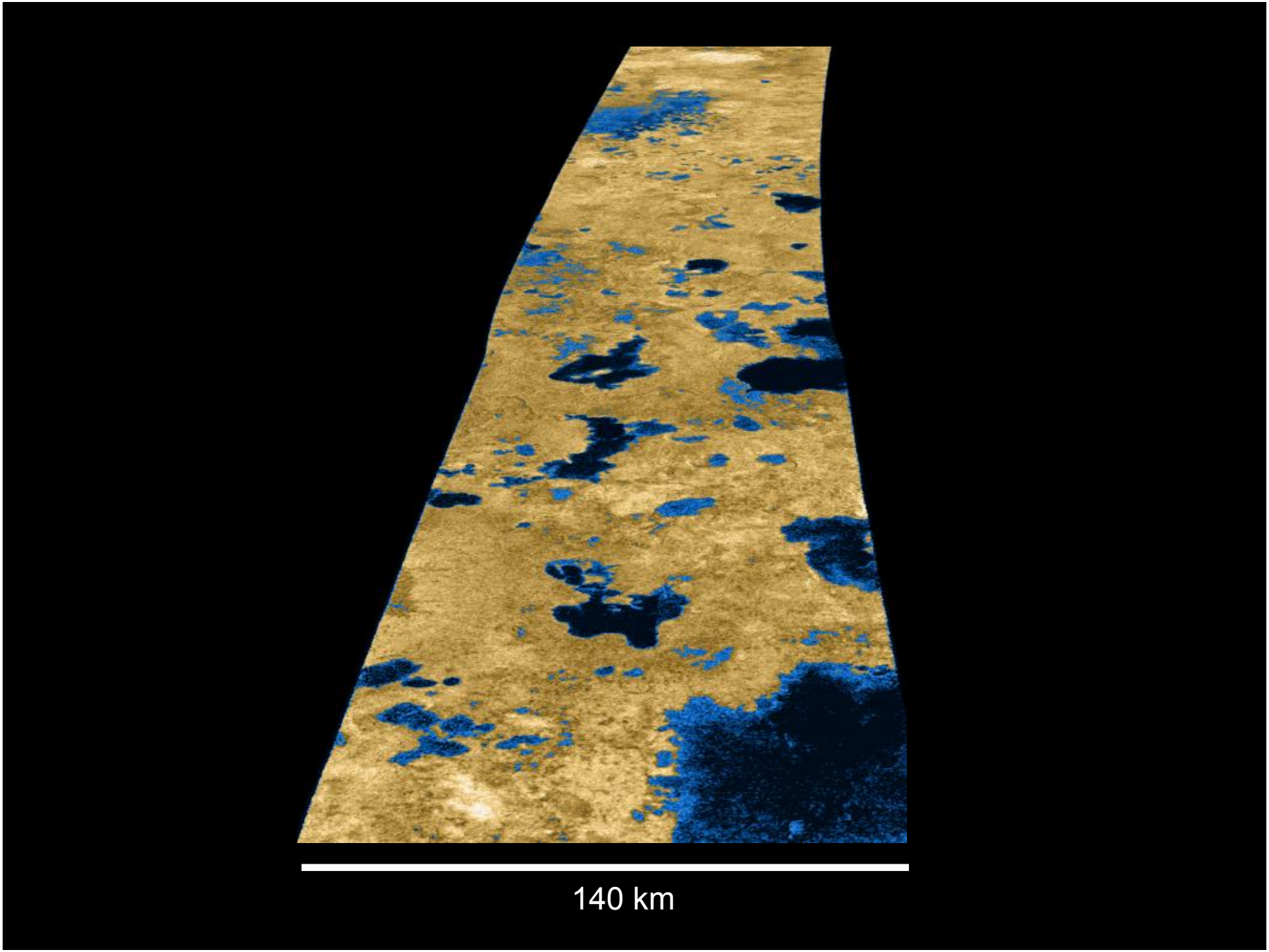
(Niemann et al. 2010)

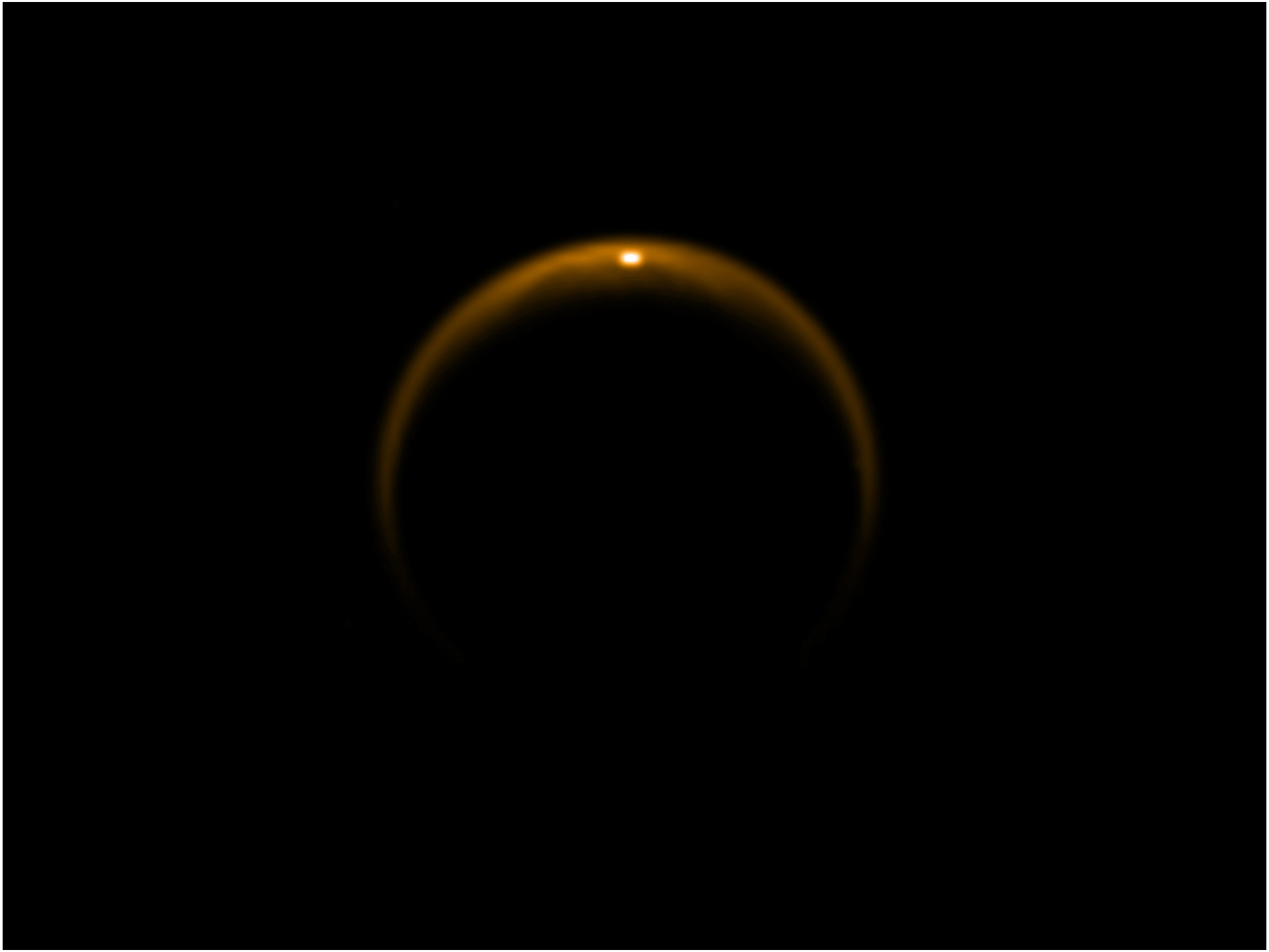
Subsaturated: relative humidity 50% just above surface

Huygens GCMS measures methane in Titan's *surface*

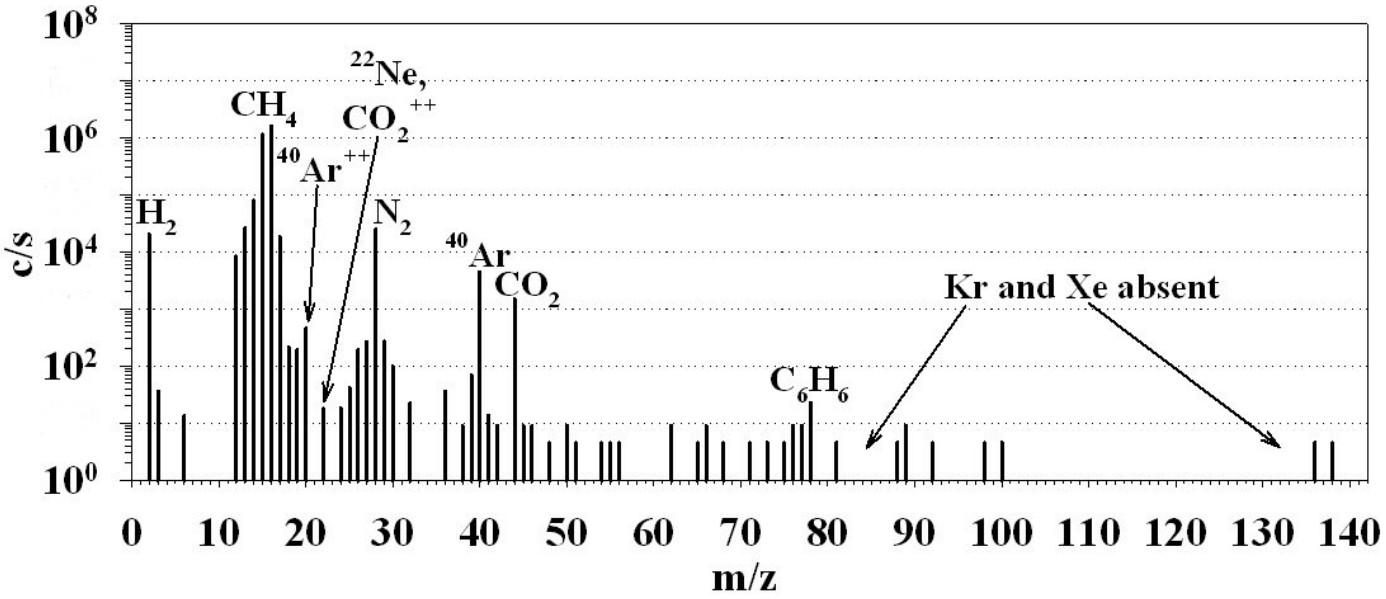


Methane mole fraction increased by 40% from surface evaporation

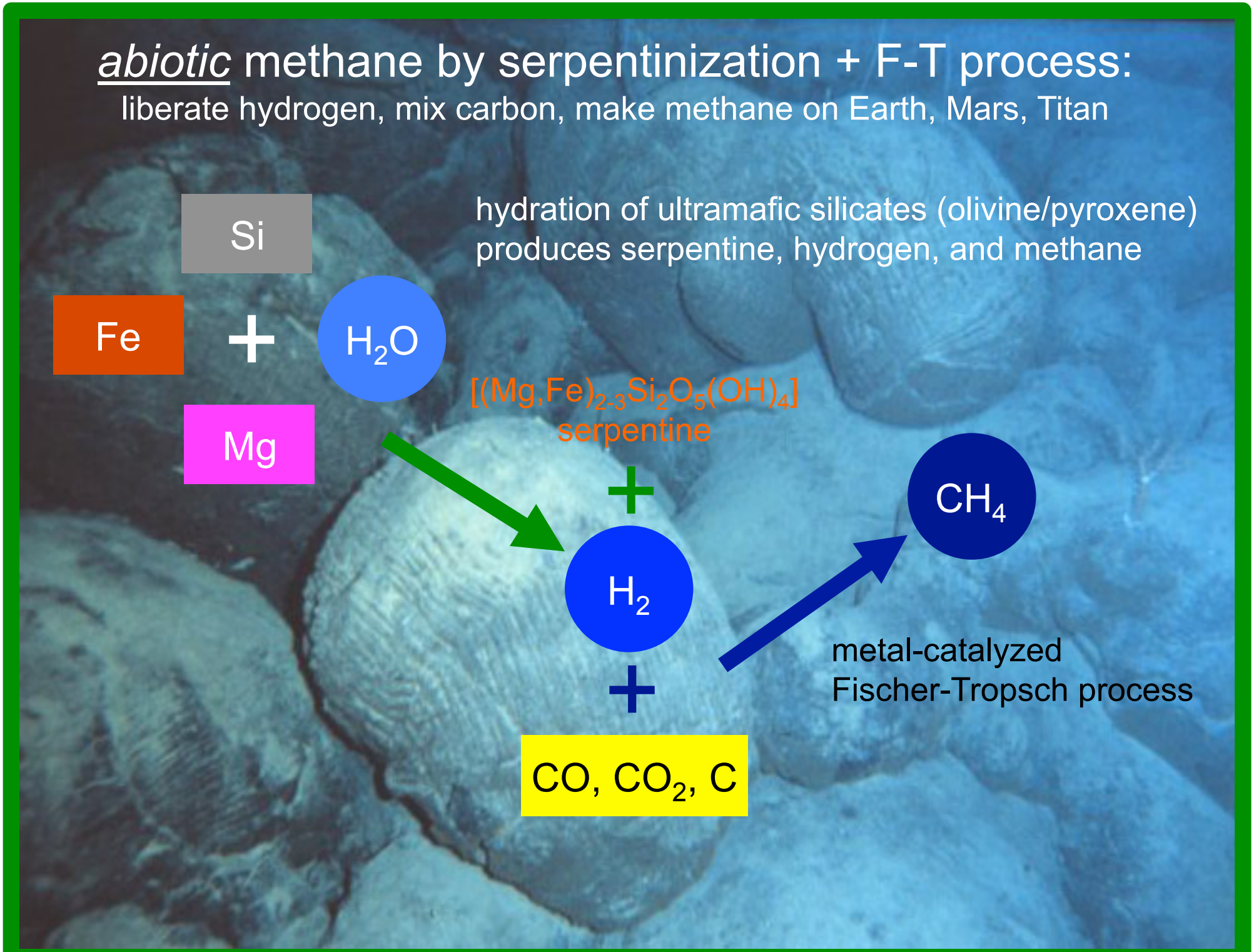

140 km



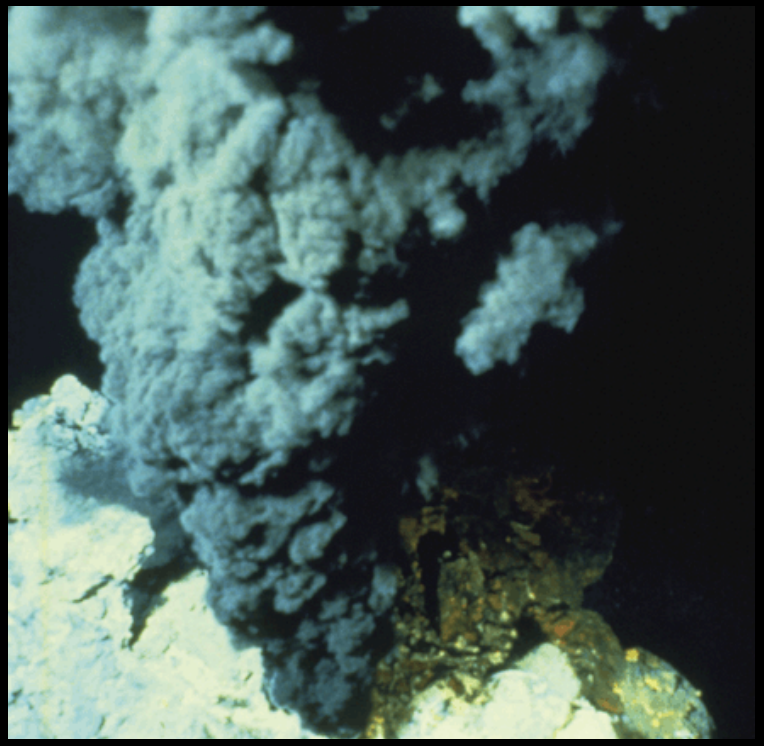
Titan's methane secondary?
clue from GCMS: Kr and Xe <10 ppbv



(Niemann et al., 2010)


abiotic methane by serpentinization + F-T process:
liberate hydrogen, mix carbon, make methane on Earth, Mars, Titan
Si
Fe
Mg
H2O
hydration of ultramafic silicates (olivine/pyroxene)
produces serpentine, hydrogen, and methane
[(Mg,Fe)2-3Si2O5(OH)4]
serpentine
H2
CH4
metal-catalyzed
Fischer-Tropsch process
CO, CO2, C

abiotic methane by *high* temperature serpentinization:
Black Smoker hydrothermal vents



Mid Atlantic Ridge

Juan De Fuca Ridge
depth 2222 m
exit temp 342 C
pressure 200 bar
chimney ht. 10 m

300-500 C, sulfur-rich, highly acidic (~lemon juice)

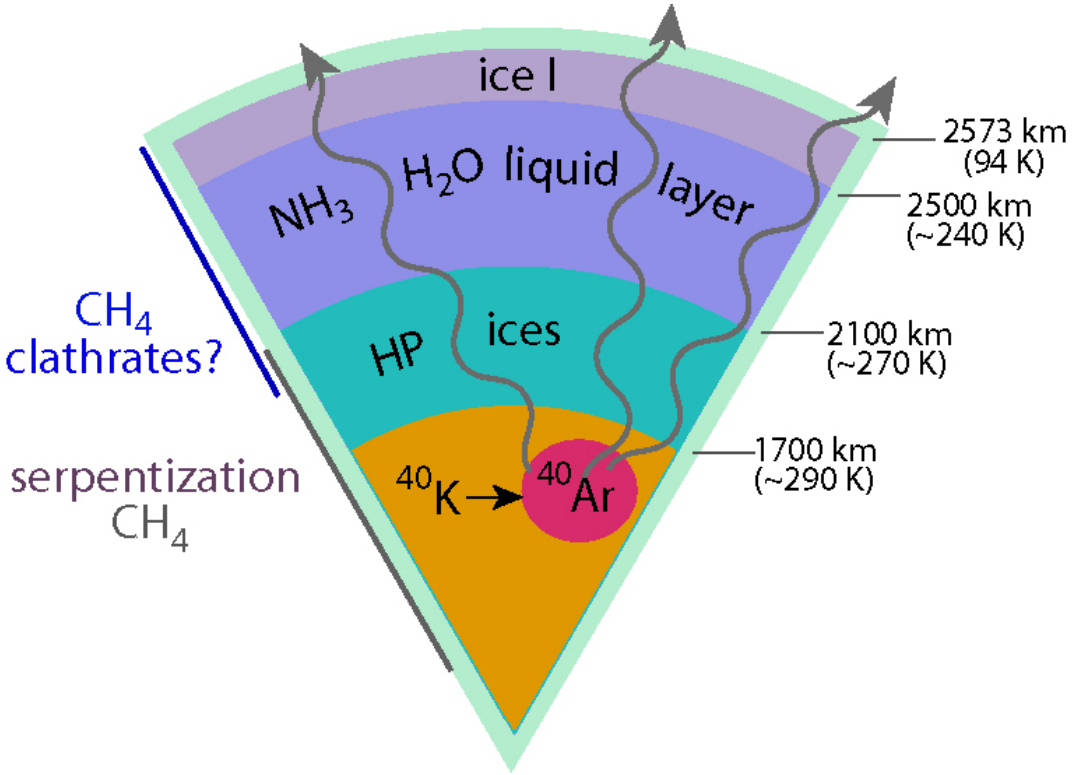
abiotic methane by *low* temperature serpentinization: ***Lost City***

- 15 km from Mid-Atlantic Ridge
- 30-90 C (120 C peridotitie)
- highly alkaline (~ammonia, milk of magnesia)
- 20 m high carbonate towers
- little sulfur minerals

Ar released from 2000 km depth at Titan!

- ^{40}Ar detection (^{40}K→^{40}Ar 1.3 Gyr half-life)
- cryovolcanism
- CO (VIMS)

→**CH_4outgassing**



(Ar data from Huygens GCMS, Niemann et al. 2005); interior structure, after Grasset et al.)

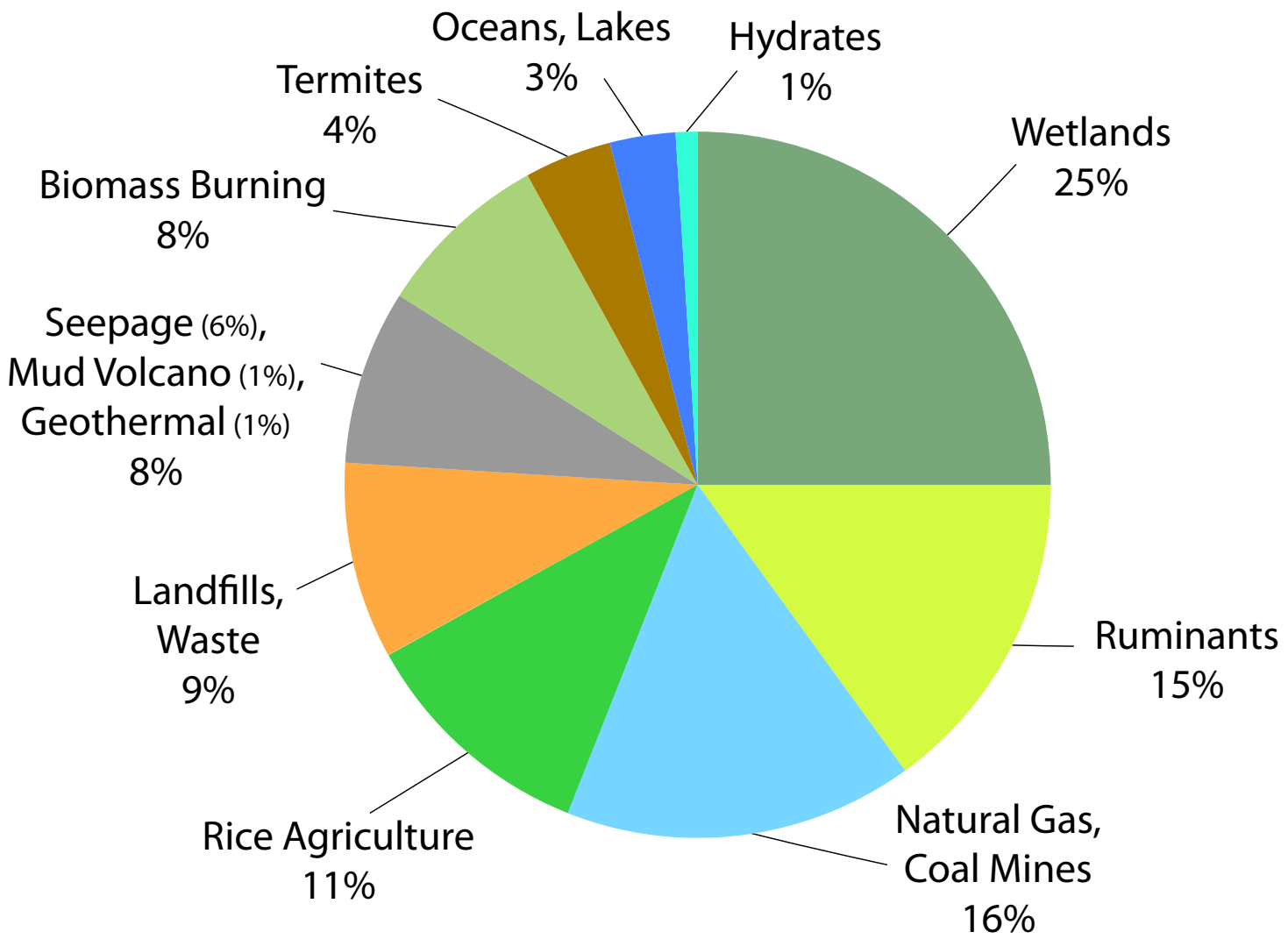
Titan's xenon and krypton hiding: methane primordial

- buried as clathrates below Titan's ocean.
  destabilization? outgassing? ^{40}Ar?

- in shallow subsurface clathrathes.
  destabilization? outgassing?

- trapped in aerosols.
  surface degassing? selective?

Biological Methane: Earth, Titan (?)



90-95% of Earth's (1775 ppbv) methane is biogenic

Titan's methane: biogenic?

medium, nutrients and energy, essential for life

- methane, not water, used as medium and solvent by Titan microbes (McKay & Smith, 2005; Schulze-Makuch & Grinspoon, 2005)

- microbes utilize H_2 and C_2H_2 as nutrients
- release CH_4 as metabolic product (McKay & Smith, 2005)

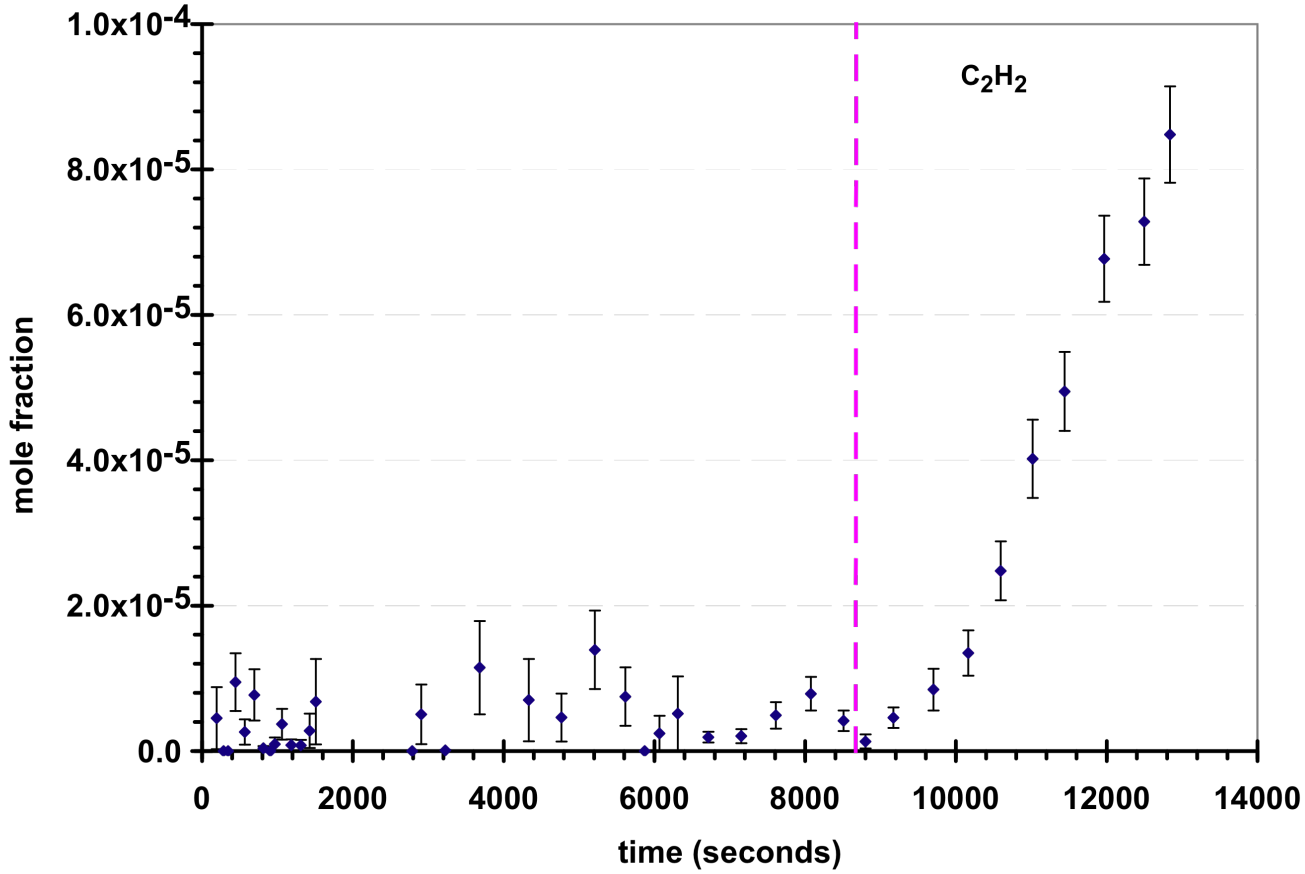
$$C_2H_2 + 3H_2 \rightarrow 2CH_4 \quad (+334 \text{ kJ/mol, ok for microbial survival})$$

→ circular argument for methane origin:
C_2H_2 and H_2 are products of CH_4

→ *depletes nutrients, not seen by GCMS:*
C_2H_2 present in surface, and *H_2 uniformly mixed*

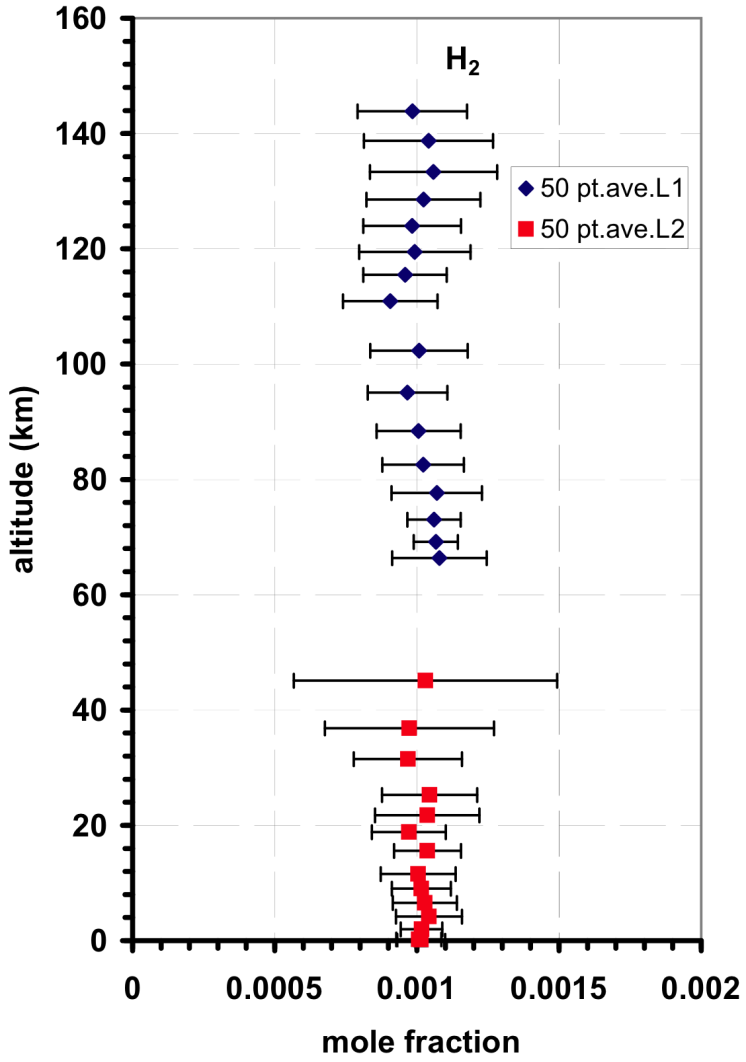
Titan's methane does not originate from microorganisms

C_2H_2 in Titan's surface – lots of it



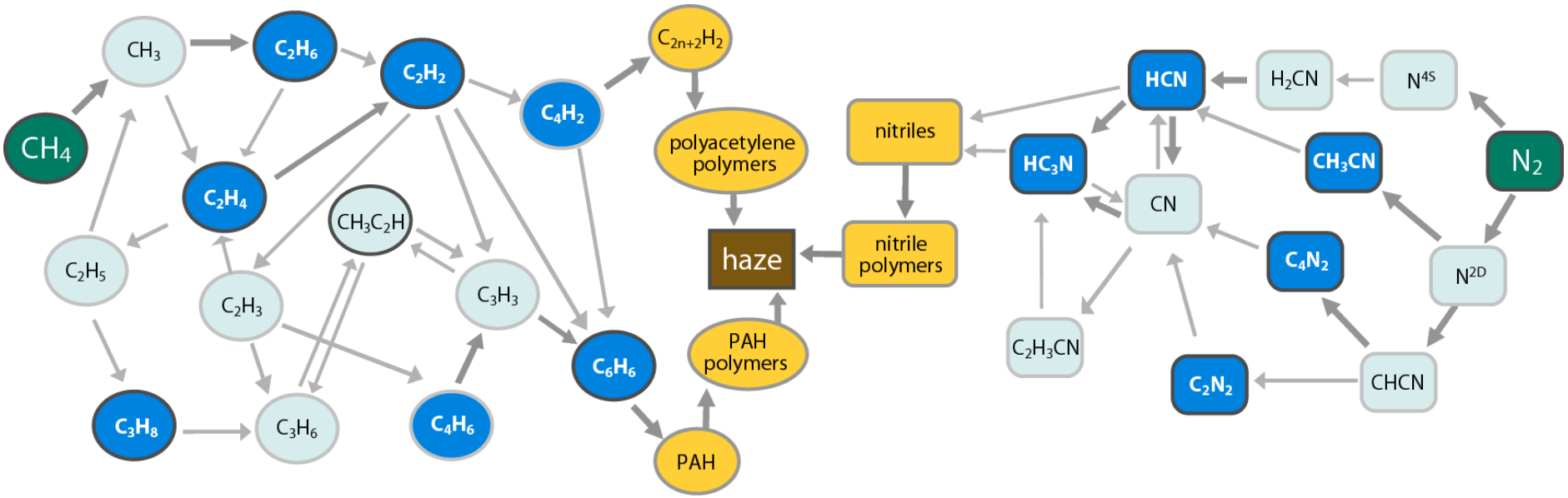
(Niemann et al., 2010)

H_2 uniformly mixed – no depletion



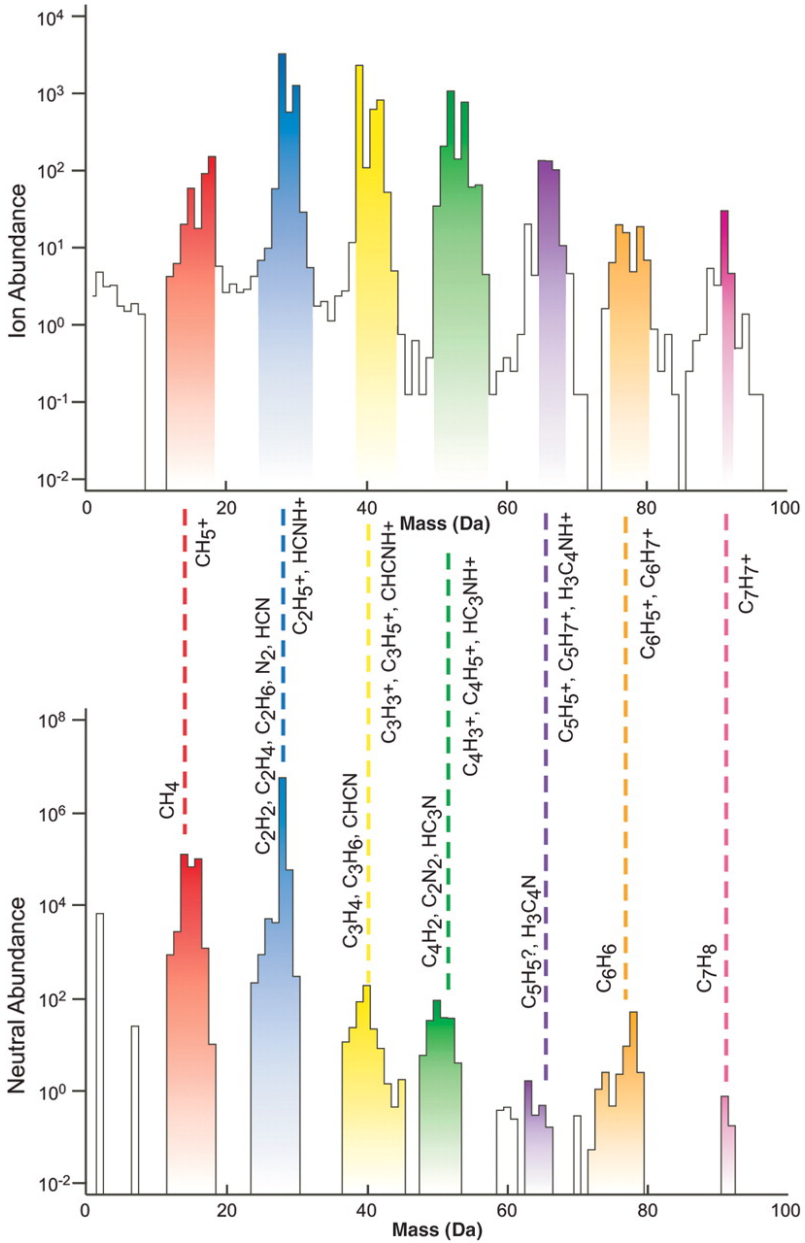
(Niemann et al., 2010)

fate of methane: hydrocarbons, nitriles, aerosols



Methane destroyed irreversibly in 10-30 Myr

(Wilson and Atreya, 2004, 2009; Atreya et al., 2006)

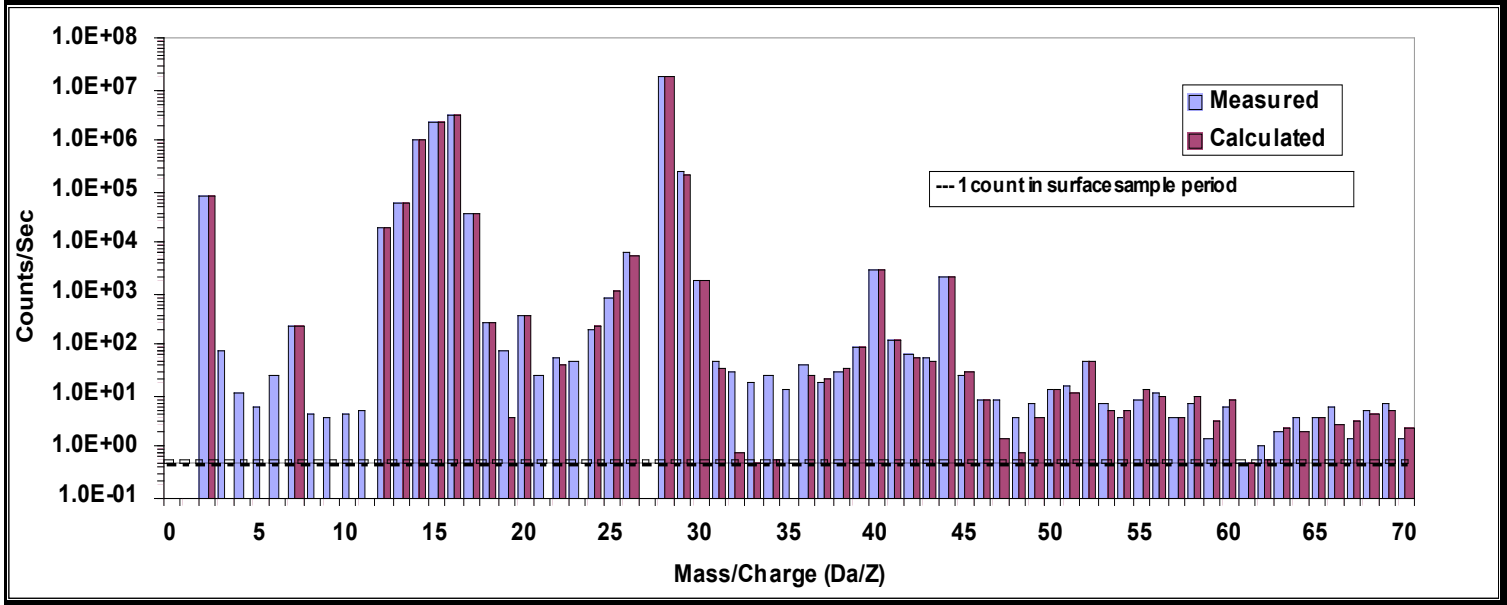


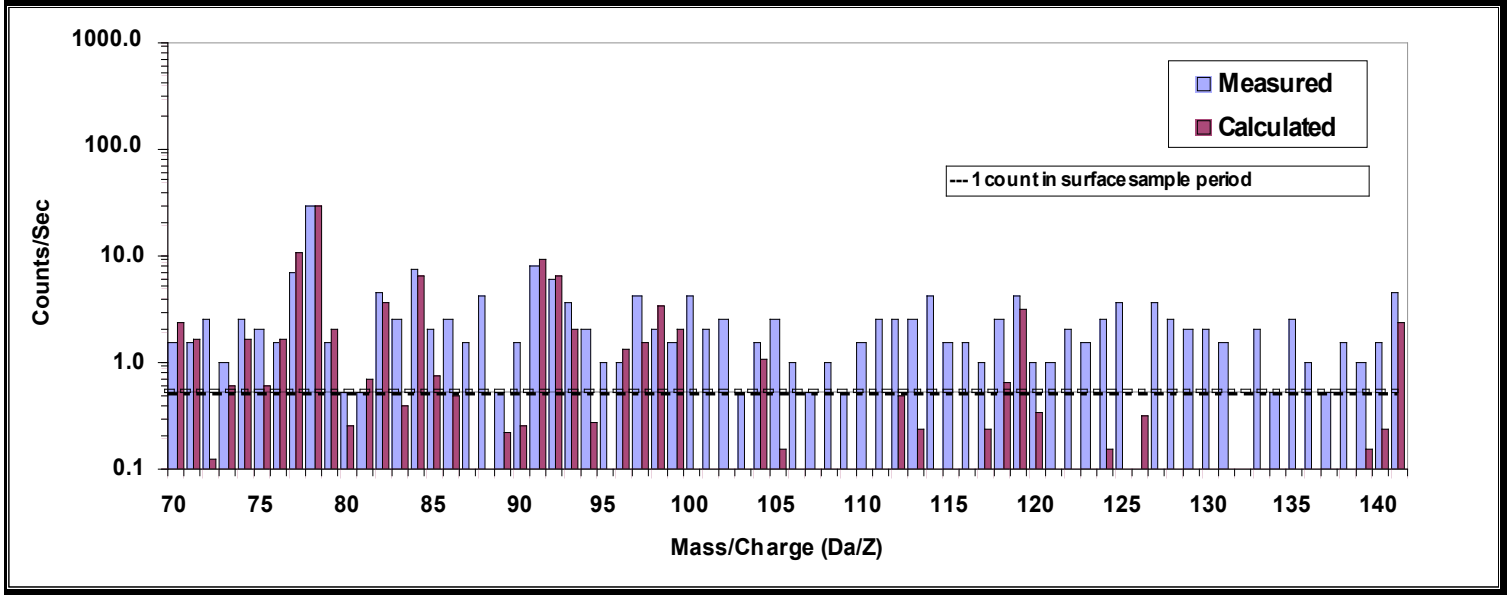
Ions

Neutrals

(Waite et al., 2007 INMS)

GCMS Measurements of Titan's Surface





Preliminary Species & Gas / N_2 Ratio

Percent

Nitrogen 28 ($^{14}N^{14}N$)

Methane (CH_4)

Nitrogen 29 ($^{14}N^{15}N$)

10,000 PPM

Hydrogen (H_2)

Carbon Monoxide (CO)

Ammonia (NH_3)

1000 PPM

Methane13 ($^{13}CH_4$)

Ethane (C_2H_6)

Acetylene (C_2H_2)

Argon40 (^{40}Ar)

Hydrogen Cyanide (HCN)

100 PPM

Carbon Dioxide (CO_2)

Nitrogen30 ($^{15}N^{15}N$)

Water (H_2O)

< 10 PPM

Allene (C_3H_4)

Propene (C_3H_6)

Butanenitrile (C_4H_7N)

Ethanedinitrile (C_2N_2)

Argon36 (^{36}Ar)

N-Butane (C_4H_{10})

Hydroperoxide ($C_5H_{12}O_2$)

Benzene (C_6H_6)

Aziridine-1-2-Buten-1-yl ($C_6H_{11}N$)

Diacetylene (C_4H_2)

N-Ethyl-2-Methylallylamine ($C_6H_{13}N$)

2-Propyn-1-amine (C_6H_7N)

Cyclobutylamine (C_4H_9N)

Cyclohexylguanidine ($C_7H_{15}N_3$)

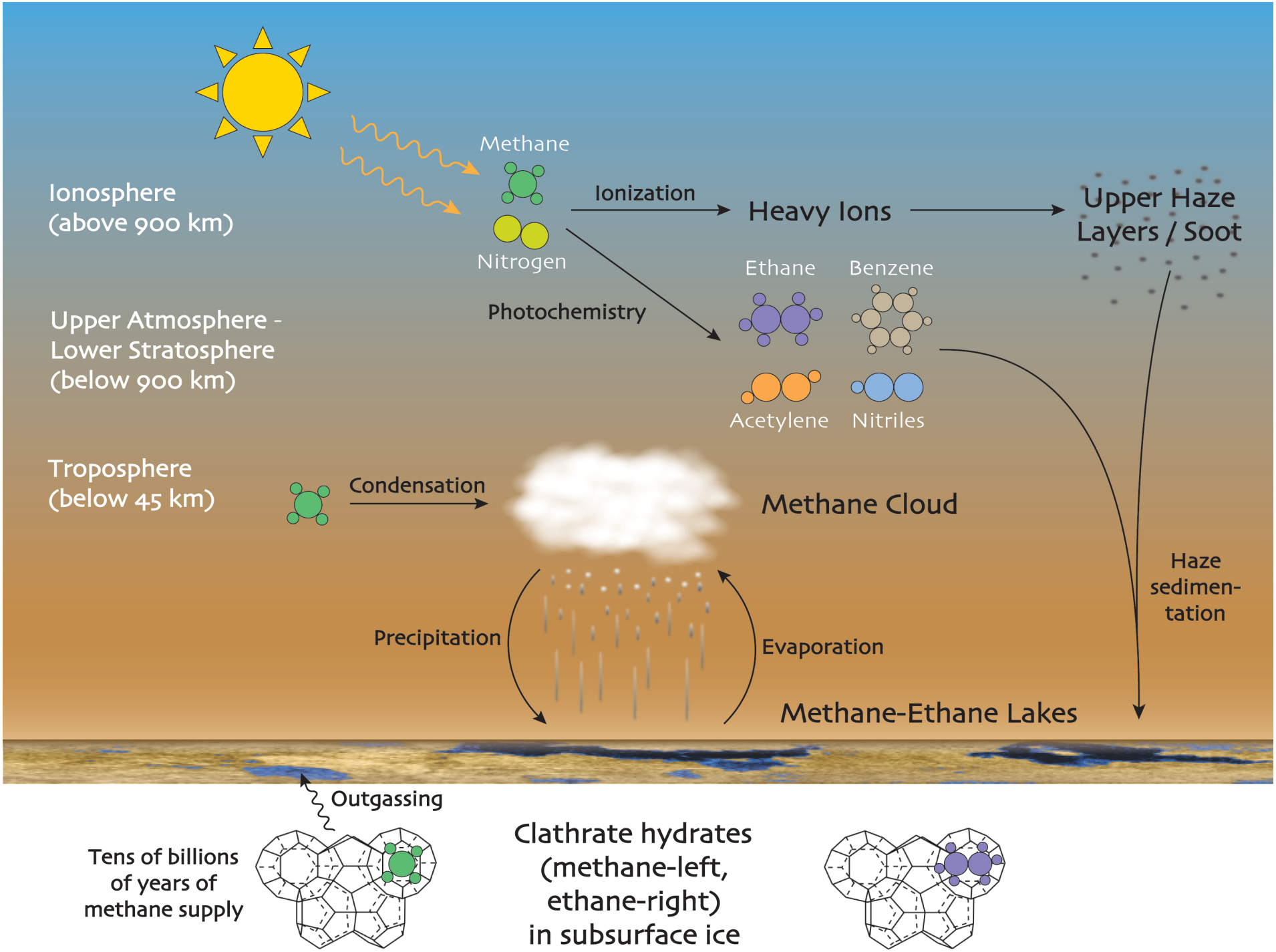
Aziridine-1-phenyl (C8H9N)

2-Cyanosuccinonitrile ($C_5H_3N_3$)

1-Pentene (C_6H_{12})

Acetonitrile (C_2H_3N)

Propanenitrile (C_5H_9N)


Ionosphere
(above 900 km)
Methane
Nitrogen
Ionization
Heavy Ions
Upper Haze
Layers / Soot
Ethane
Benzene
Photochemistry
Upper Atmosphere -
Lower Stratosphere
(below 900 km)
Acetylene
Nitriles
Troposphere
(below 45 km)
Condensation
Methane Cloud
Haze
sedimen-
tation
Precipitation
Evaporation
Methane-Ethane Lakes
Outgassing
Tens of billions
of years of
methane supply
Clathrate hydrates
(methane-left,
ethane-right)
in subsurface ice

Take Home

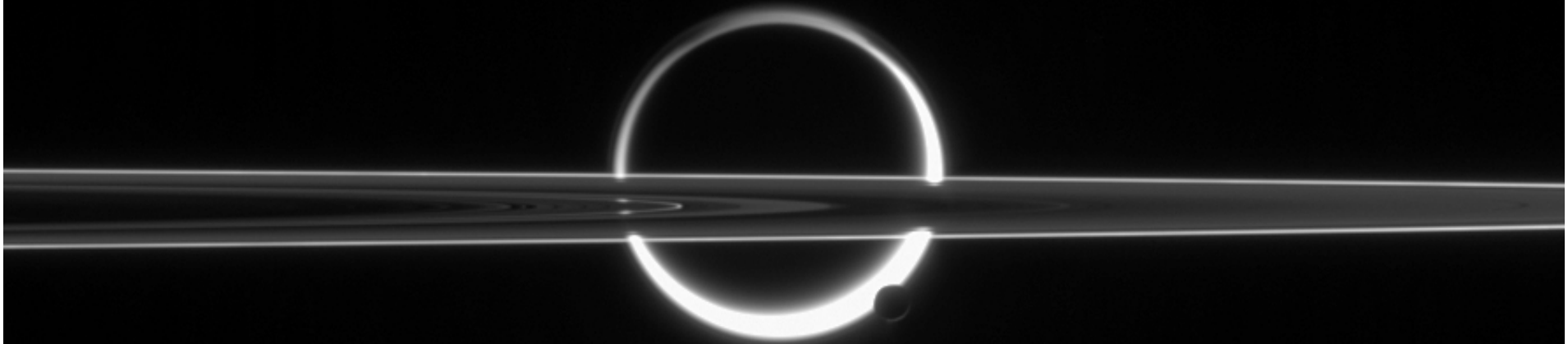
- *Nitrogen* originates from ammonia photolysis
- Impacts & endogenesis less important for N_2
- *Methane* crucial to N_2 atmosphere
- CH_4 originates from geologic, primordial, & endogenic, processes, in TBD amounts
- *Methane cycle* is similar to the Earth's hydrological cycle, but with longer dynamical, circulation, and seasonal time scales
- No energy crisis on Titan!


Surface is key to Titan's mysteries !

Hot Titans

- *Saturn system migration post-accretion*
- N_2 atmosphere survives, $v_T < v_{esc}$ for $T<10^4$ K
- Combustion chemistry dominates photochemistry
- Carbon soot, and possibly sulfur allotropes (S_2-S_8), sulfuric acid (H_2SO_4) and CHNOPS aerosols replace haze of hydrocarbons and nitriles
- Hot surface and cryogenic upper atmosphere replace cold atmosphere and colder surface
- Titan begins to look more like Venus than Earth

?



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pdf’s of publications: homepage (google sushil atreya)

Scientific American article: ask me

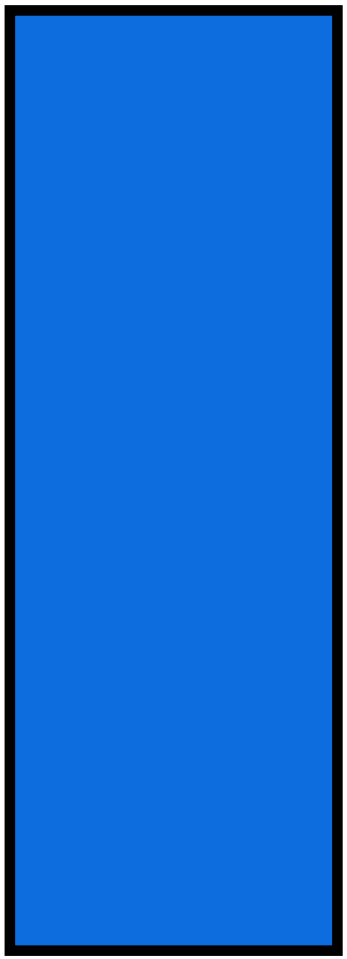
Additional Slides

Titan Through Time

- Christiaan Huygens discovers Titan, 1655
- Comas Sola sees limb darkening (atmosphere?), 1908
- Gerard Kuiper detects methane from Kitt Peak, 1944
- Voyager spacecraft detects nitrogen, 1980, and finds
  - atmospheric pressure = 1.5 bars
  - surface temperature = 93.5 K (-179.5 °C, -291 °F)
  - atmospheric density = 4.4 x Earth's atmosphere
  - haze (this image)
- Cassini-Hyugens spacecraft arrives at Saturn, 30 June 2004
- Huygens lands on Titan 14 January 2005
- Titan Facts:
  - mass = 1.35x 10^{23} kg (0.023 x Earth's)
  - diameter = 5150 km (1.48 x Moon; 1.06 x Mercury; 0.98 Ganymede)
  - density = 1.88 g/cm^3 (50% ice, 50% rock)
  - distance from Saturn = 1,211,850 km ($20R_s$, 3.2 x Earth-Moon distance)
  - orbital period = 15.94 days – synchronous (Earth's moon 27.3 days)

Characteristic	Titan	Enceladus	Triton	Pluto	Ganymede	Io	Moon
R_{planet}	20.25 R_S	3.95 R_S	14.33 R_N	[39.53 AU]	14.99 R_J	5.9 R_J	60.27 R_E
M [10^{22} kg]	13.5	0.011	2.14	1.31	14.82	8.94	7.35
R_e [km]	2575	252	1352	1150	2631	1815	1738
ρ [kg/m^3]	1880	1608	2064	2050	1936	3570	3340
g [m/s^2]	1.35	0.12	0.78	0.66	1.43	1.796	1.622
T_O [days]	--	--	--	[248 yr]	--	--	--
T_S [days]	15.95	1.37	5.877	[6.38]	7.16	1.769	27.322
i [deg]	0.33	0.02	157	17.14	0.20	0.04	5.9
e [deg]	0.029	0.005	0.000	0.25	0.001	0.0041	0.05
A	0.2	0.99 (bond) 1.4 (geometric)	0.76	0.44 – 0.61	0.4	0.63	0.12
v_e [km/s]	2.64	0.235 $v_T(N_2) > v_e$	1.50	1.1	2.75	2.56	2.38
Surface T [K]	94	114-157	38	40	110	130	40-396
Surface P [mb]	1500	Plume	0.016	0.058 (var)	negligible	(3 - 40) x 10^{-6}	negligible
Atmosphere	**N_2, CH_4**	H_2O, CO_2, CO, NH_3 (?), **N_2** (?) **CH_4**	**N_2**, **CH_4**	**N_2**, **CH_4**, CO, *(H_2O-i)*	*(H_2O_2-i)*, H, O_2, O_3 traces	SO_2	H, He, Na, H_2O, traces

where are the ethane oceans?



kilometer deep ethane ocean predicted by models where ethane (C_2H_6) was essentially the terminal product of CH_4 photochemistry *(Lunine et al., 1983*)

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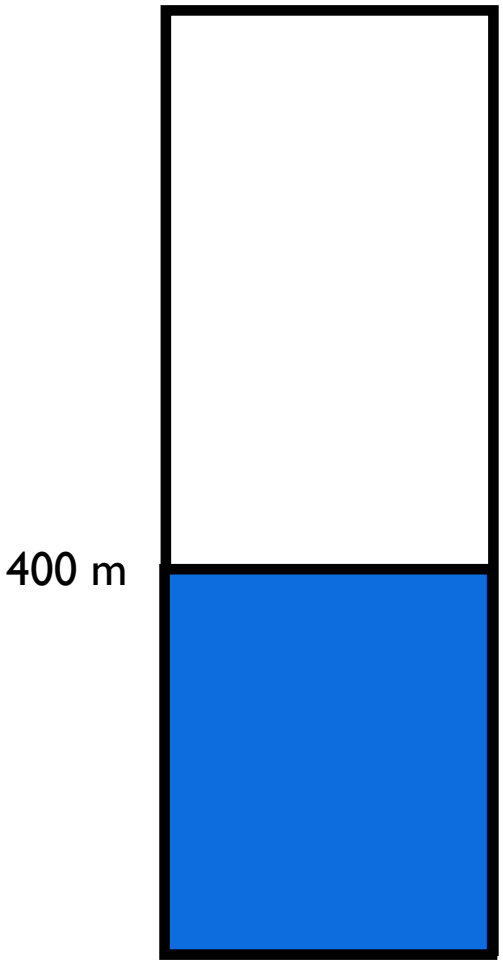

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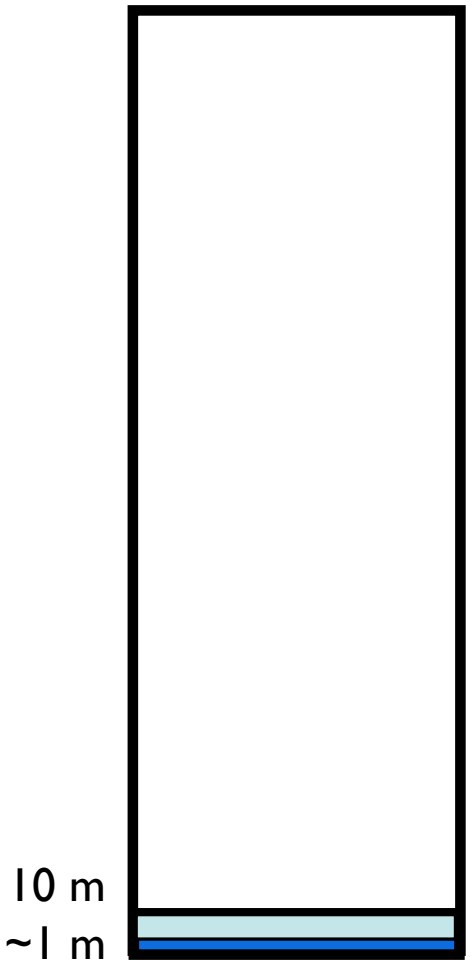
chemistry proceeds beyond C_2H_6 to C_6H_6, PAH's…,

vertical mixing in stratosphere smaller *(Atreya et al., 2006; Wilson & Atreya, 2009)*

where are the ethane oceans? ..



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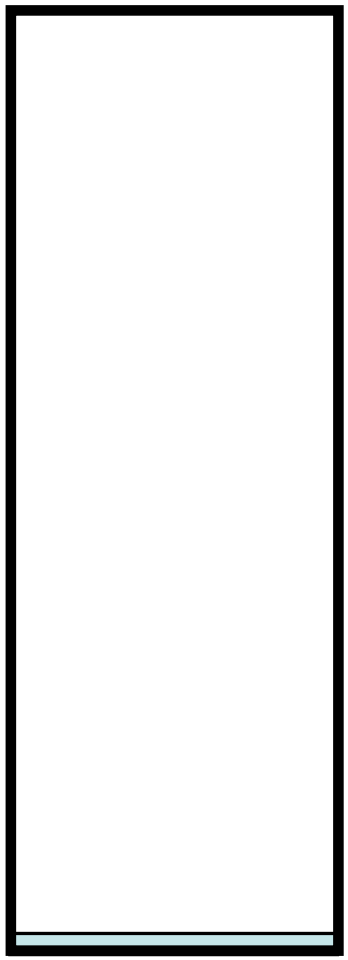
chemistry proceeds beyond C_2H_6 to C_6H_6, PAH's…,

vertical mixing in stratosphere smaller *(Atreya et al., 2006; Wilson & Atreya, 2009)*

episodic outgassing of methane; most recent 600 Myr ago *(Tobie et al., 2006)*

← with 30 Myr CH_4 lifetime

where are the ethane oceans?…



kilometer deep ethane ocean predicted by models where ethane (C_2H_6) was essentially the terminal product of CH_4 photochemistry *(Lunine et al., 1983)*

chemistry proceeds beyond C_2H_6 to C_6H_6, PAH's…,

vertical mixing in stratosphere smaller *(Atreya et al., 2006; Wilson & Atreya, 2009)*

episodic outgassing of methane *(Tobie et al., 2006)*

→ ethane sequestered as clathrate in subsurface, if water-ammonia ocean was periodically in contact with the surface

→ lakes of methane/ethane, as (liq) ethane is fully miscible in (liq) methane *(Lunine & Atreya, 2008; Brown et al., 2008)*

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