Titan: The Solar System's Abiotic Petroleum Factory

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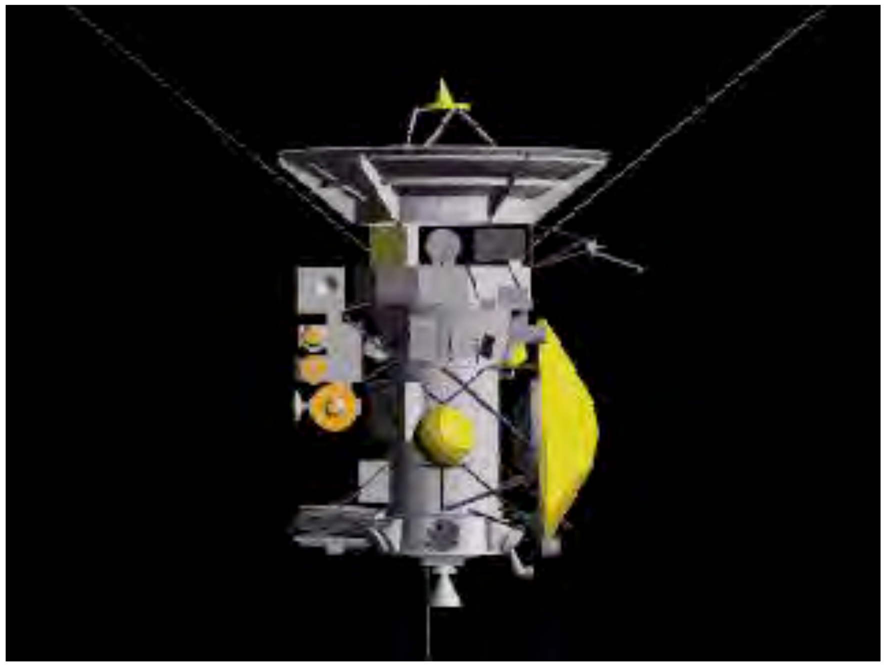
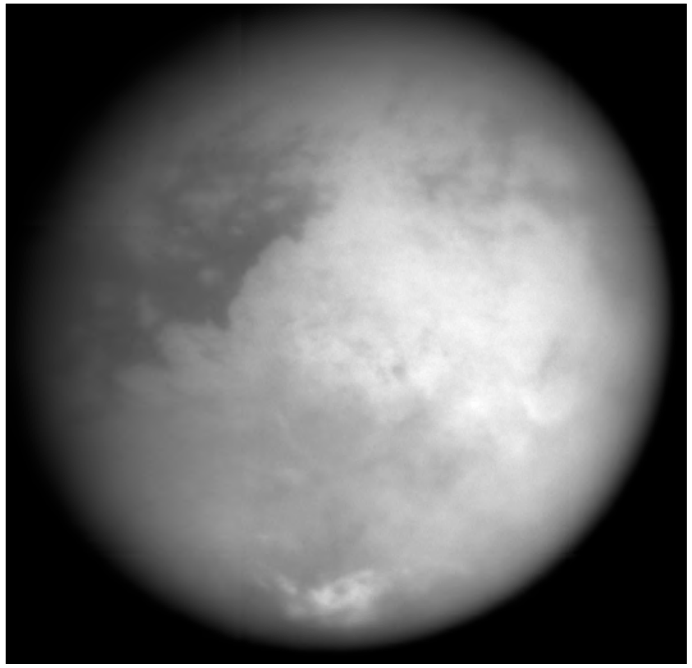
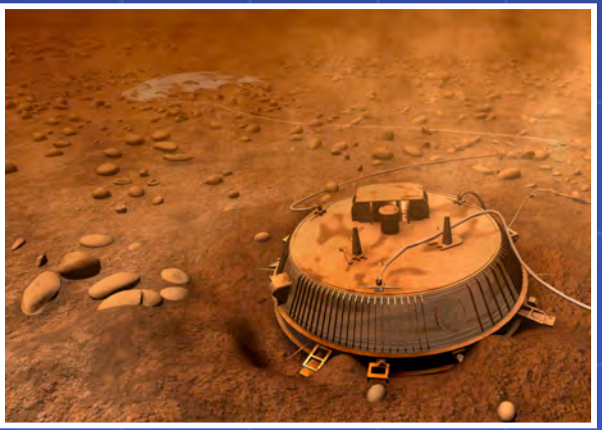
Motivation for Titan Studies:

- **Titan's atmosphere is similar to Earth's early atmosphere**
- **Titan may help us understand the origin of life in the solar system**
- **Titan may help us unlock the mysteries to organic formation in other regions of our galaxy and universe**

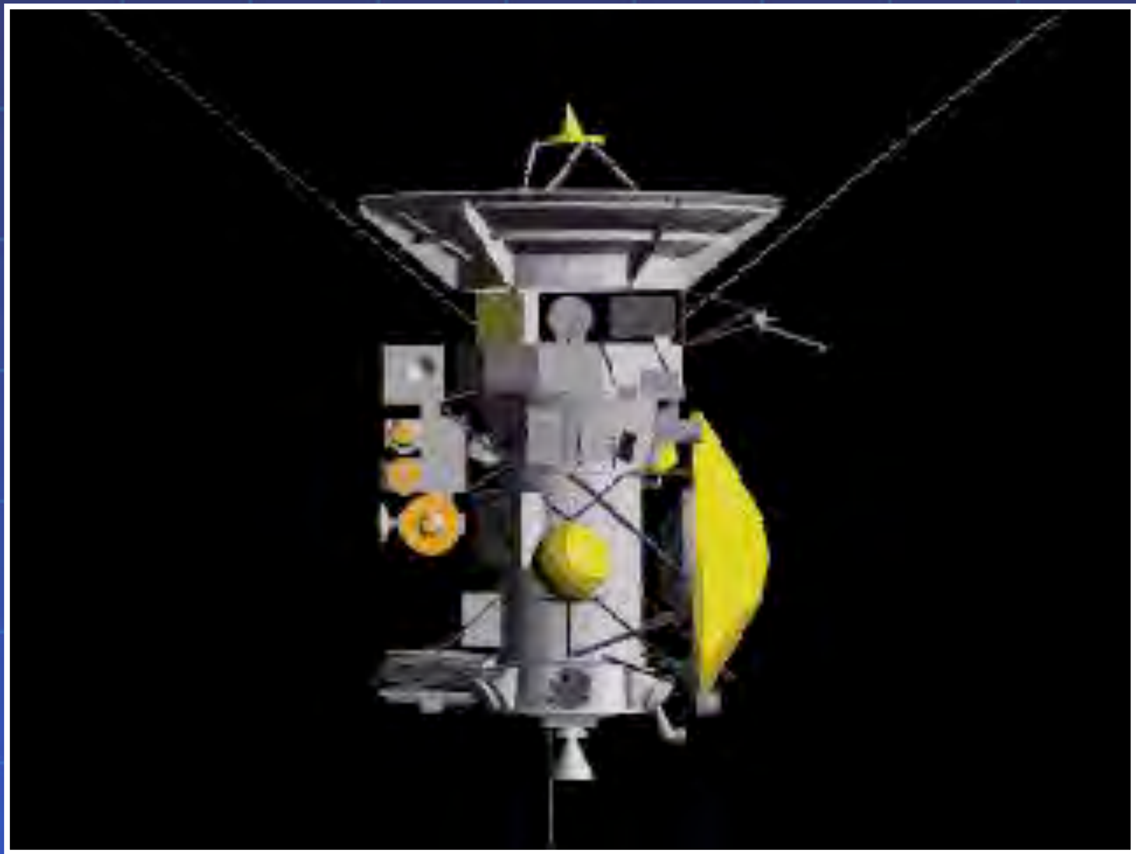
Cassini Huygens Measurements



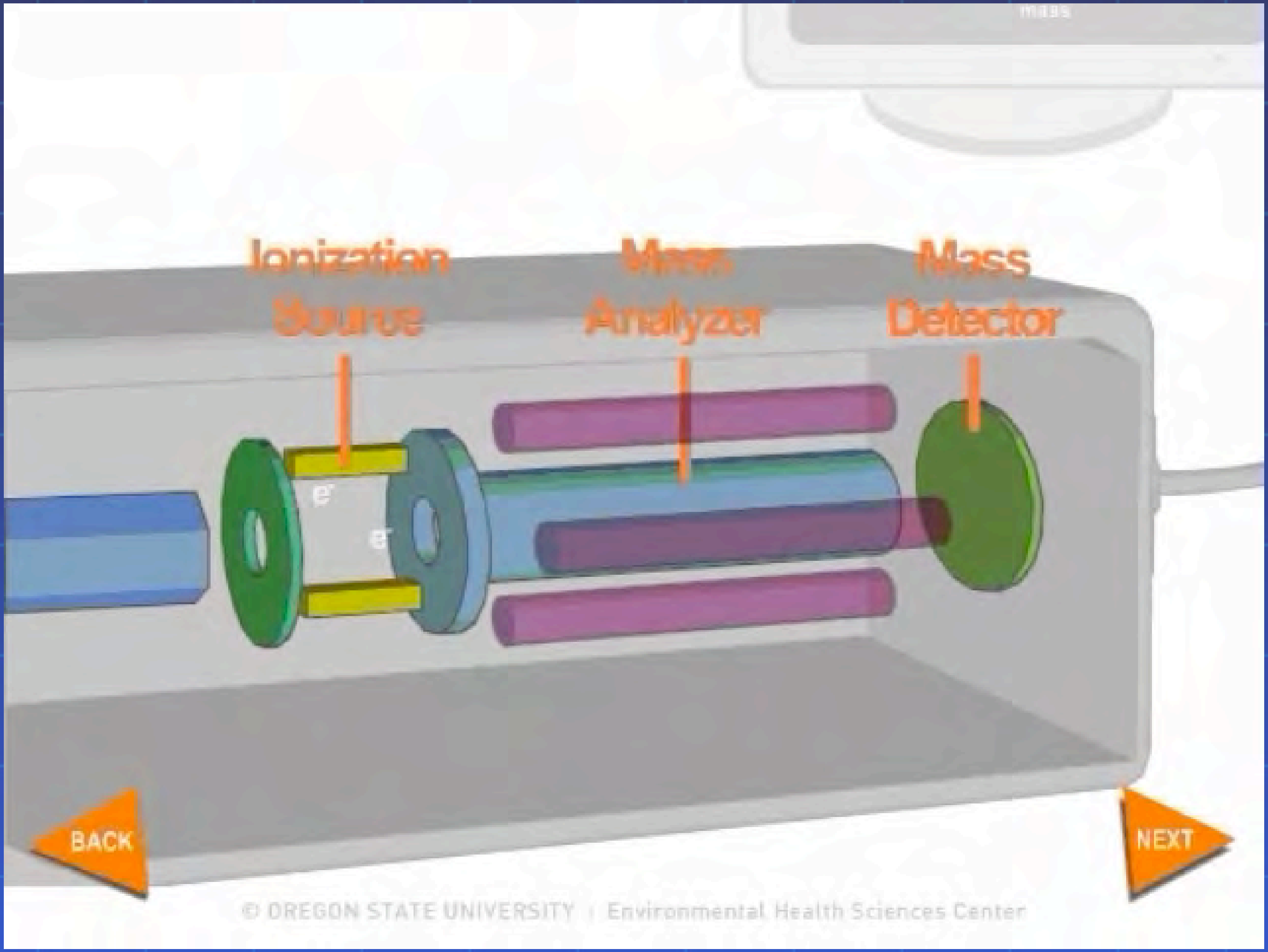




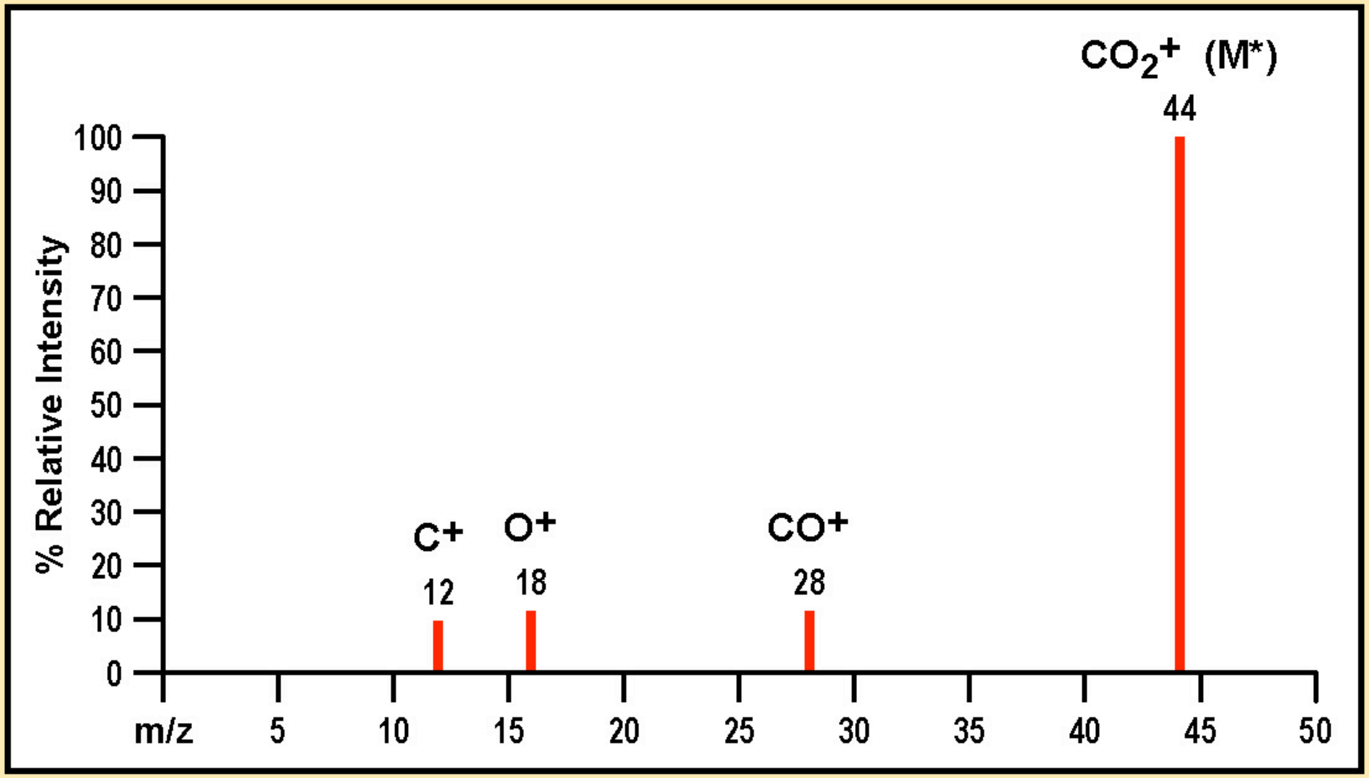
Orbiter In Situ Measurements



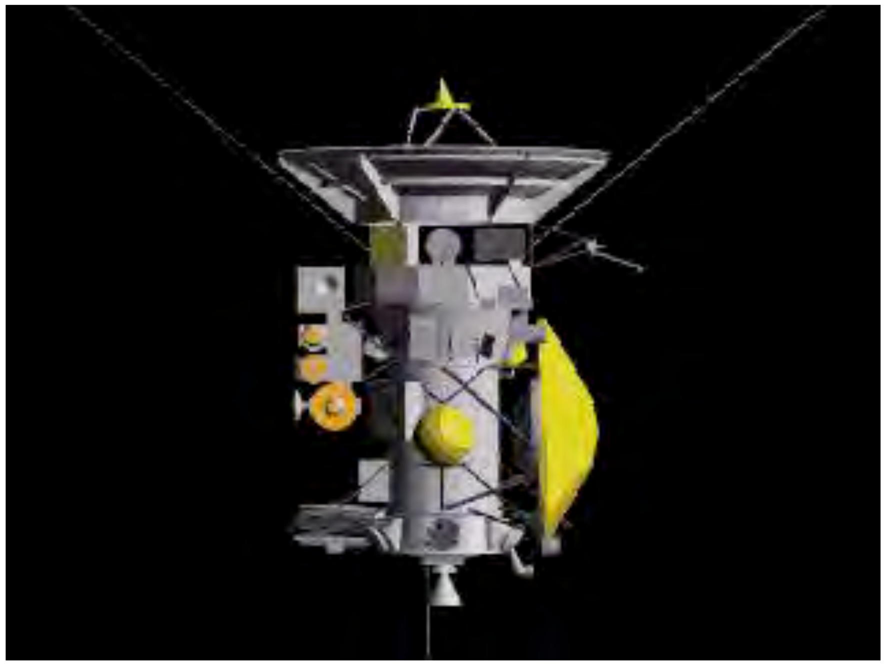
Mass Spectrometry

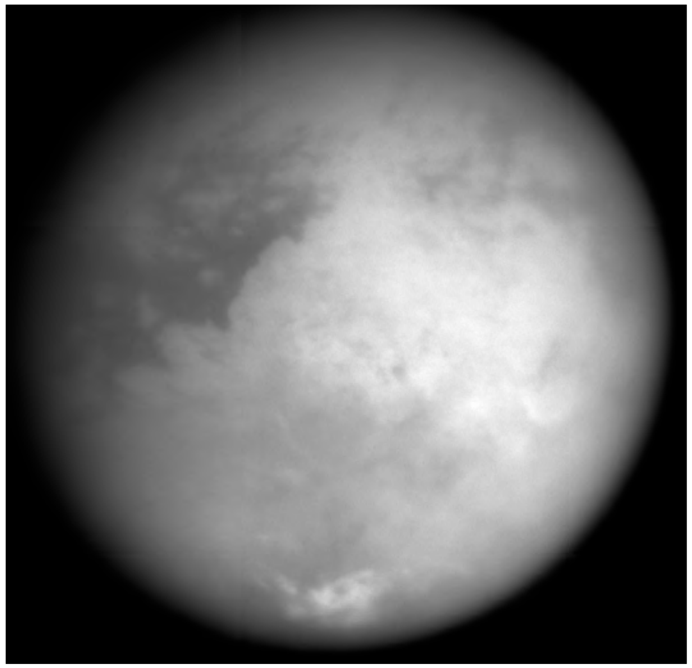


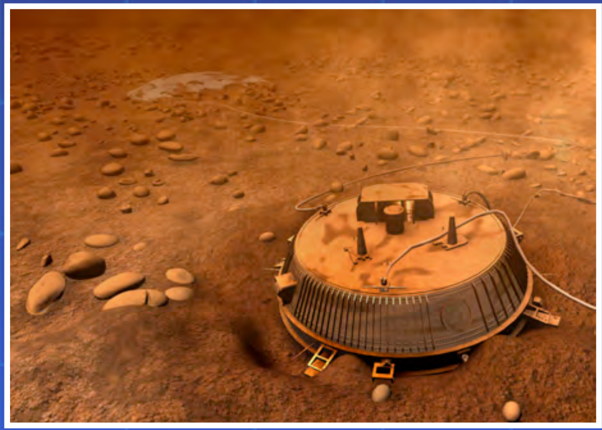
Mass Spectrometry



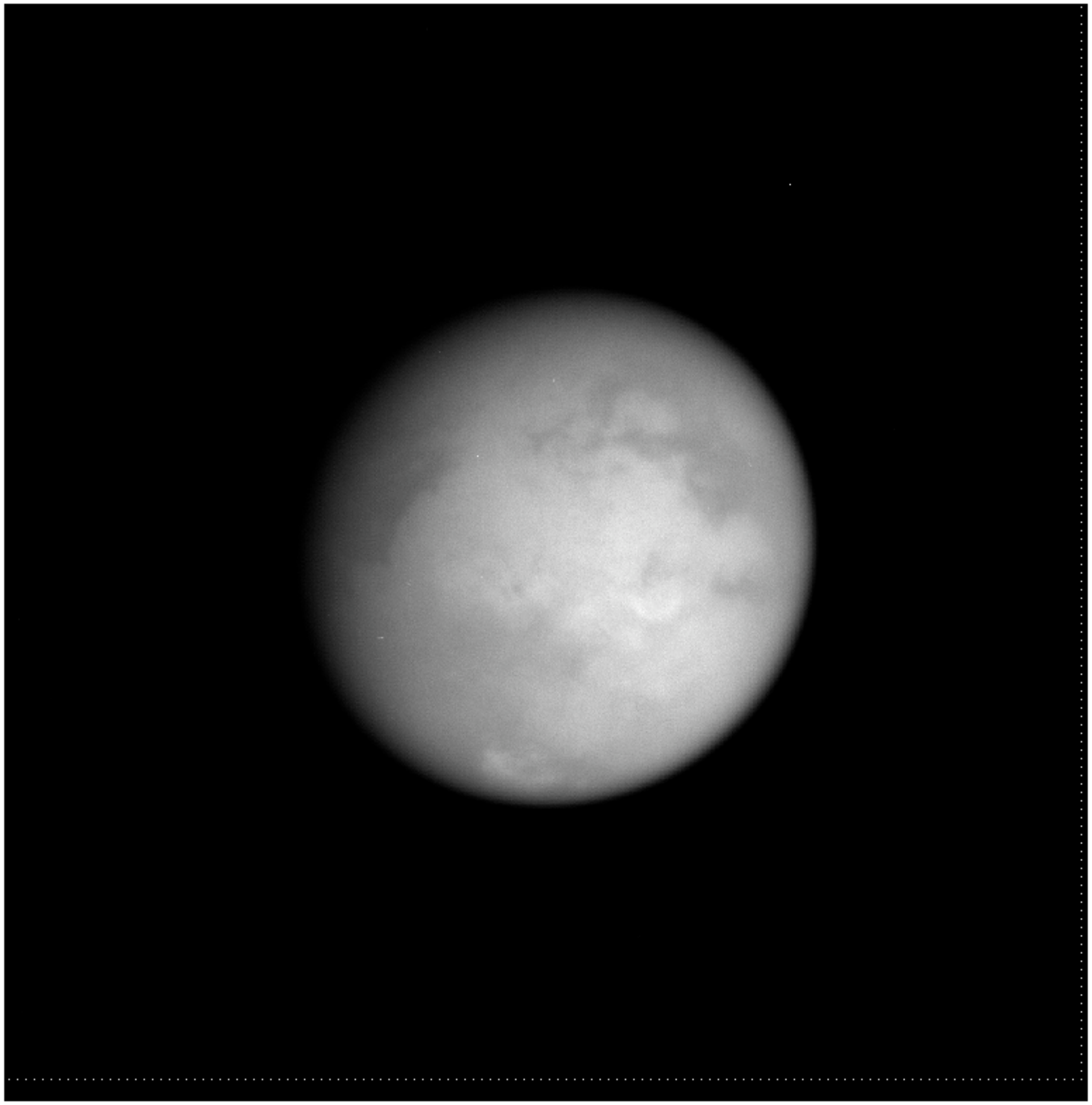
Cassini Huygens Measurements



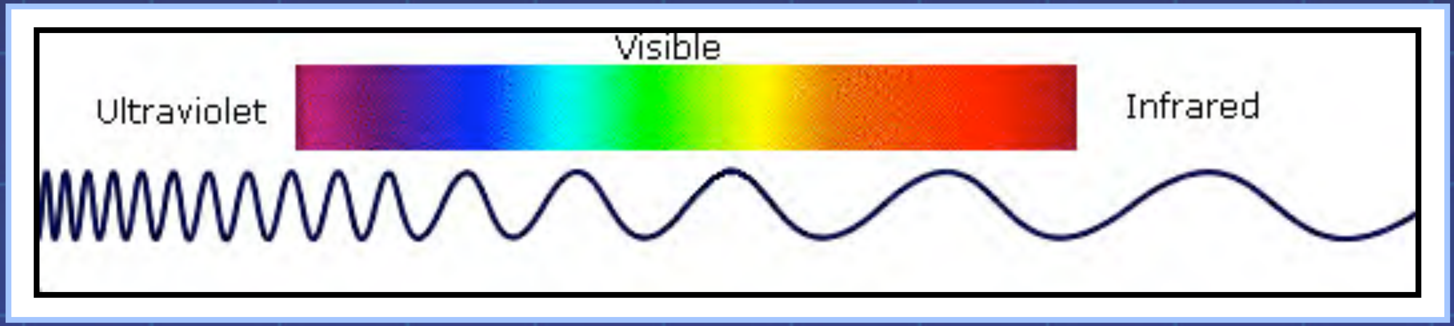


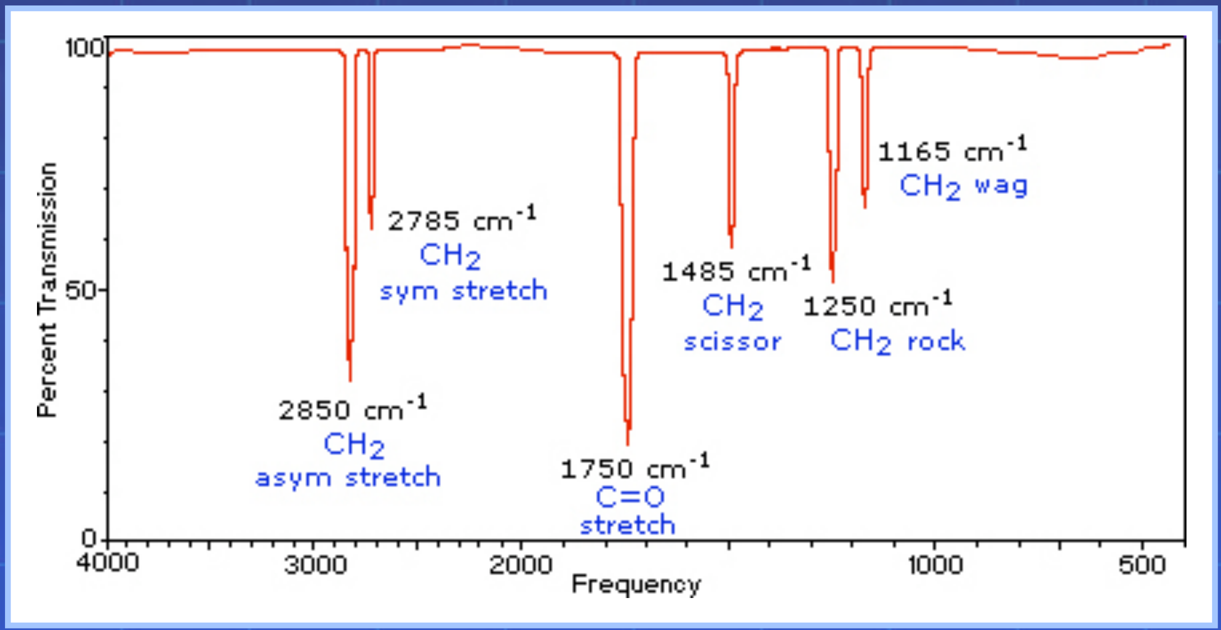


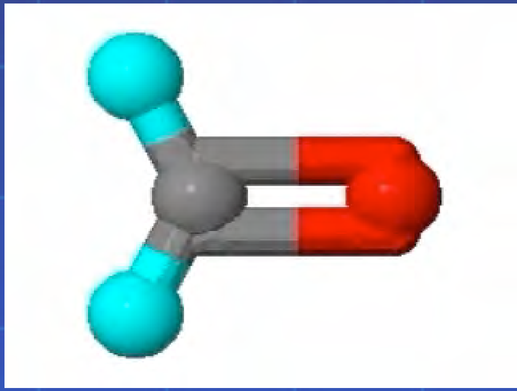
Orbiter Remote Sensing Measurements



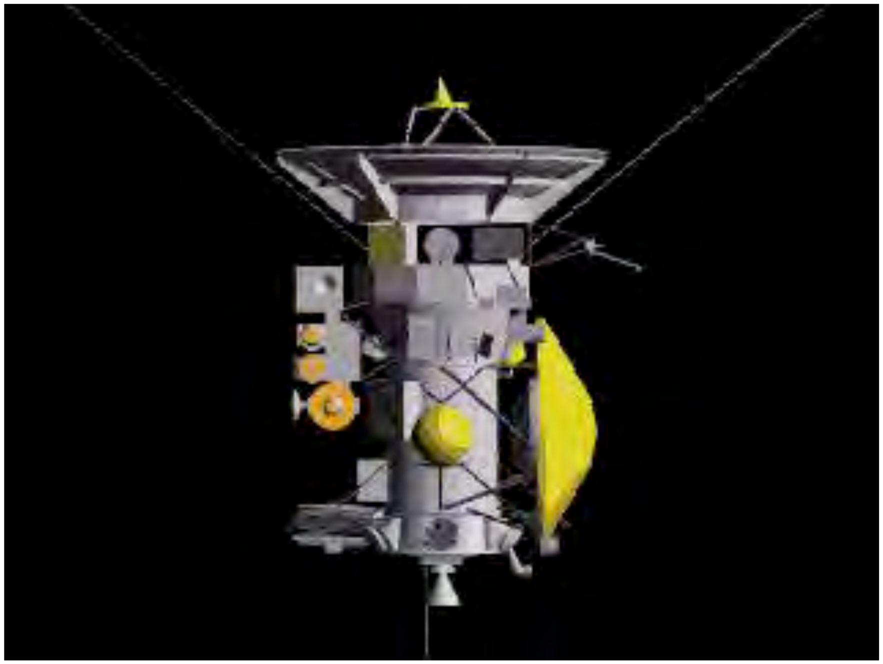
Infrared Spectrometry

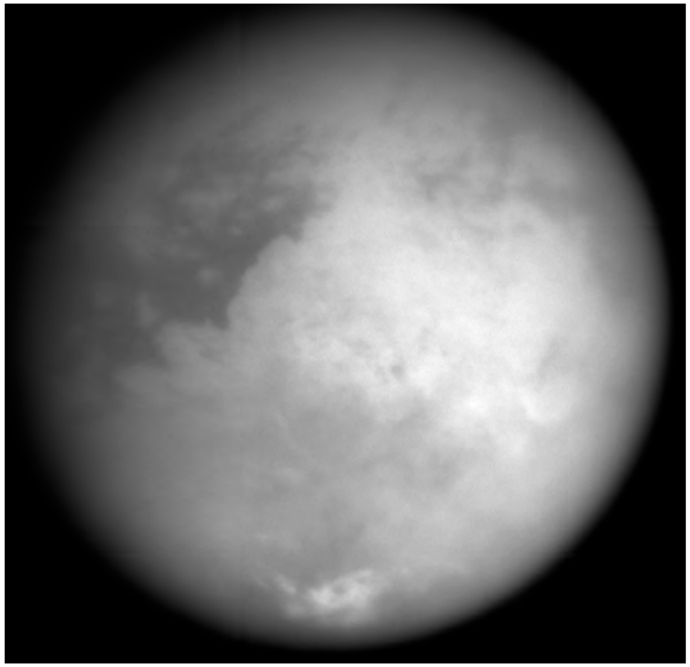


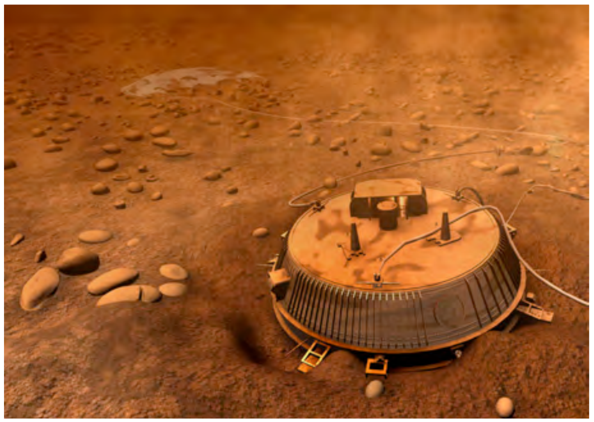




Cassini Huygens Measurements

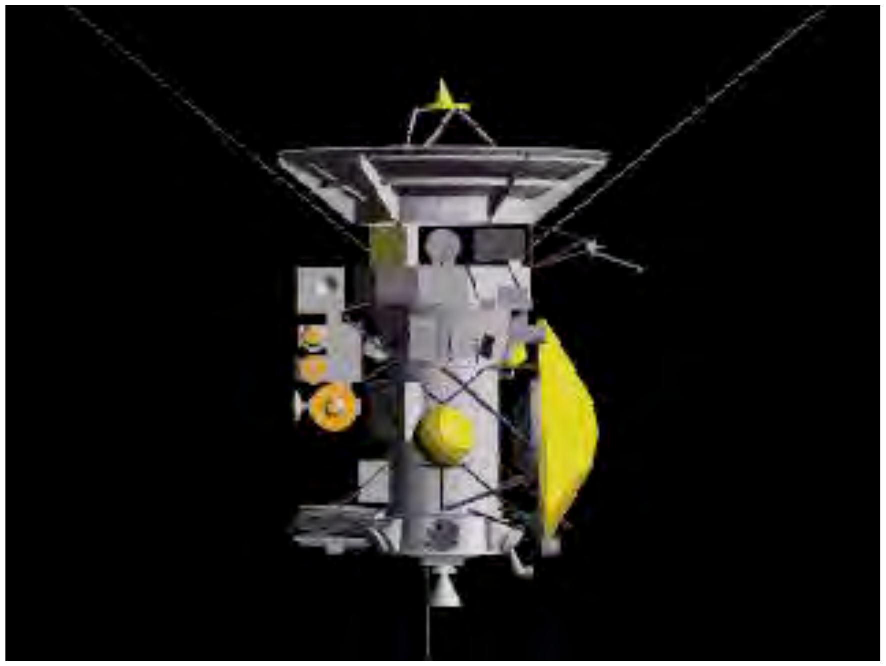


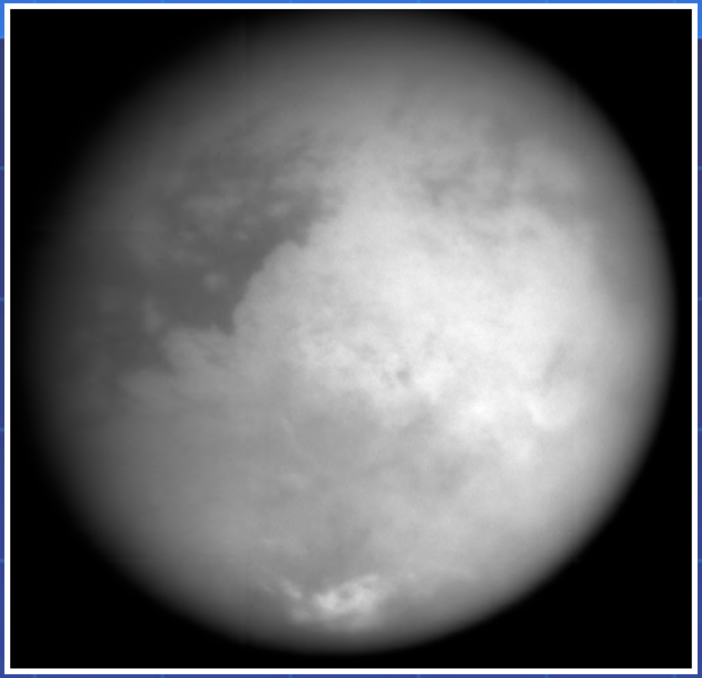


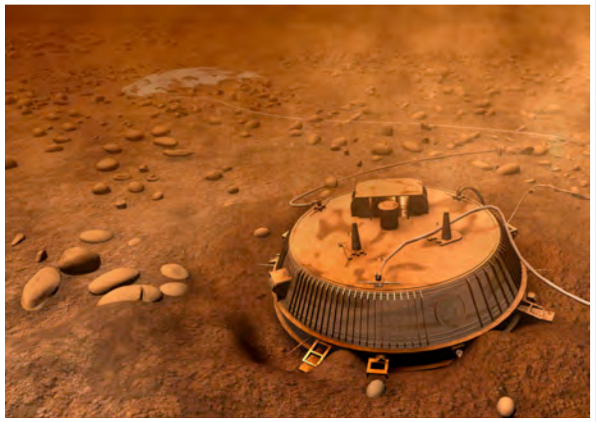


Probe Measurements

Cassini Huygens Measurements

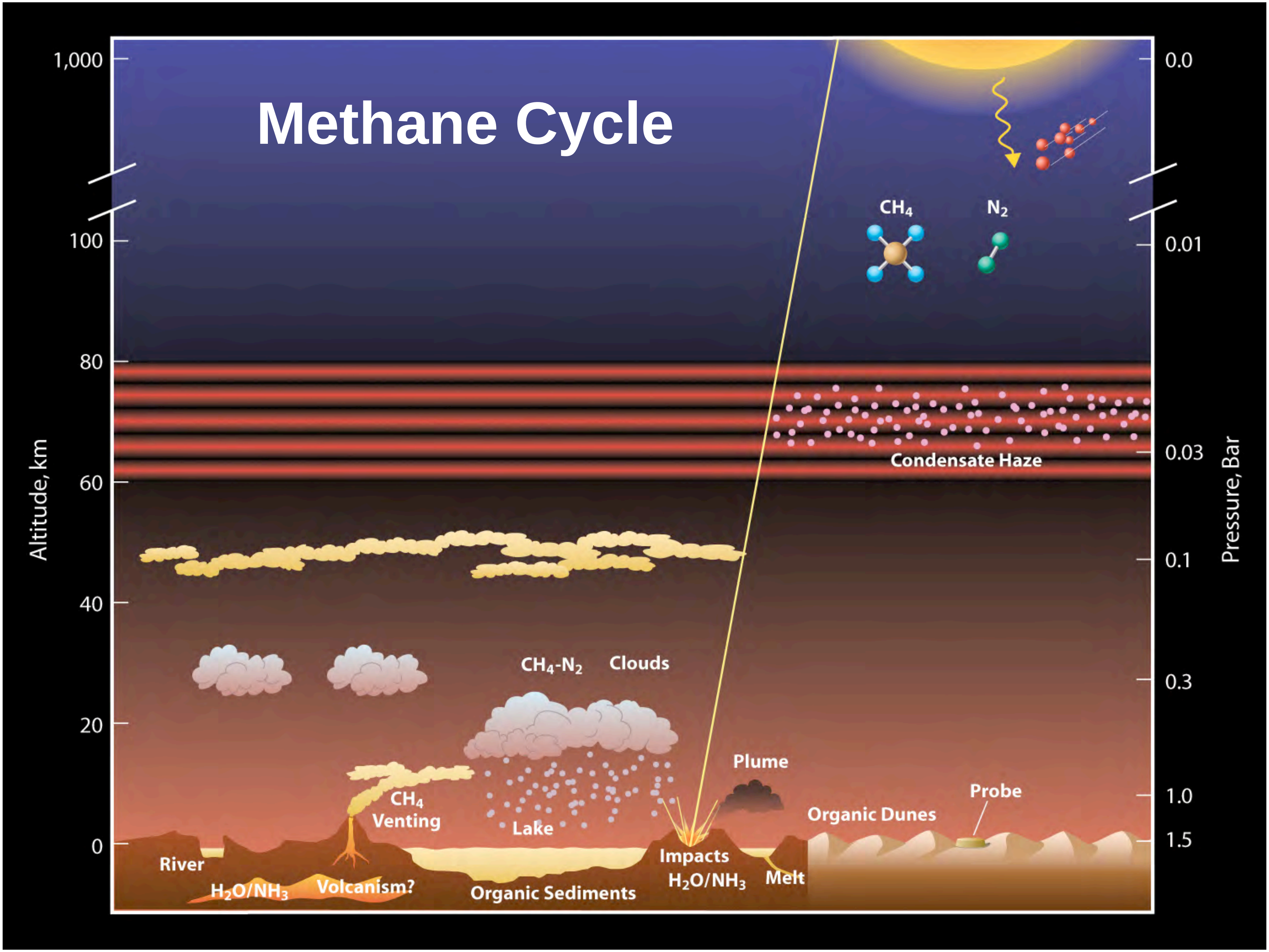






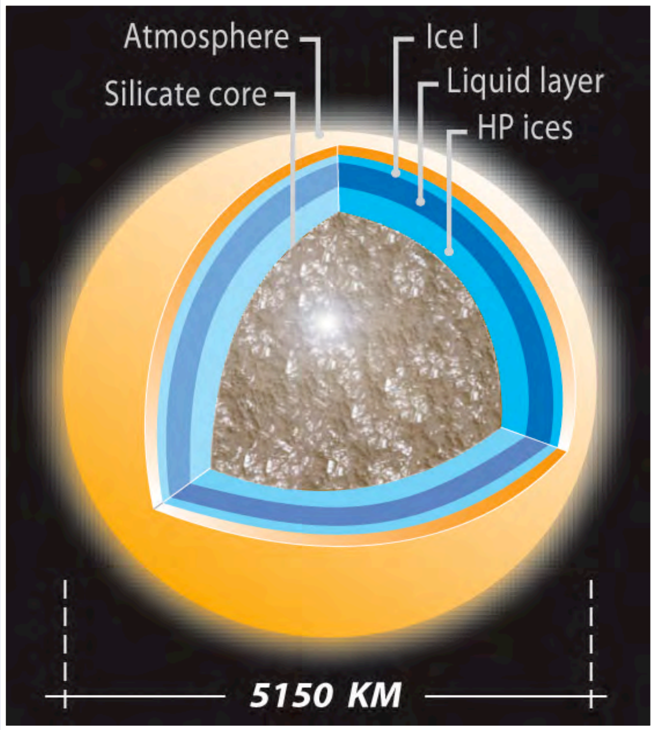
Orbiter Radar Measurements

Methane Cycle



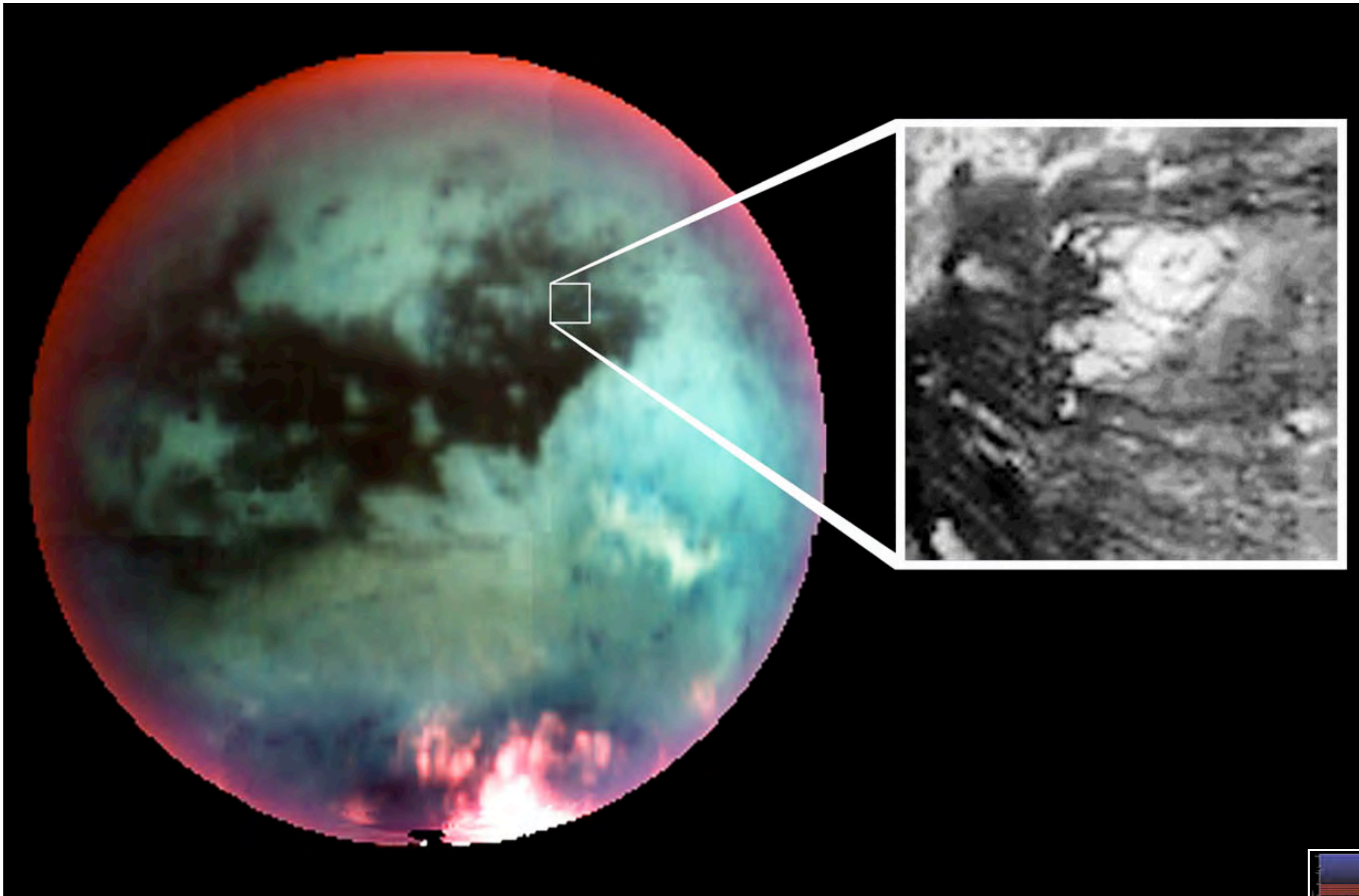
Possibilities for Titan Geology: What's Cryo-Volcanism?

- Large rocky core; layers of liquid, water ice
- Abundant ammonia; melting point of water ice lowered by ±100ºC
- Tectonism could breach crust; fluid could reach surface
- Ammonia-water "cryo-lava" would erupt as gelatinous mass

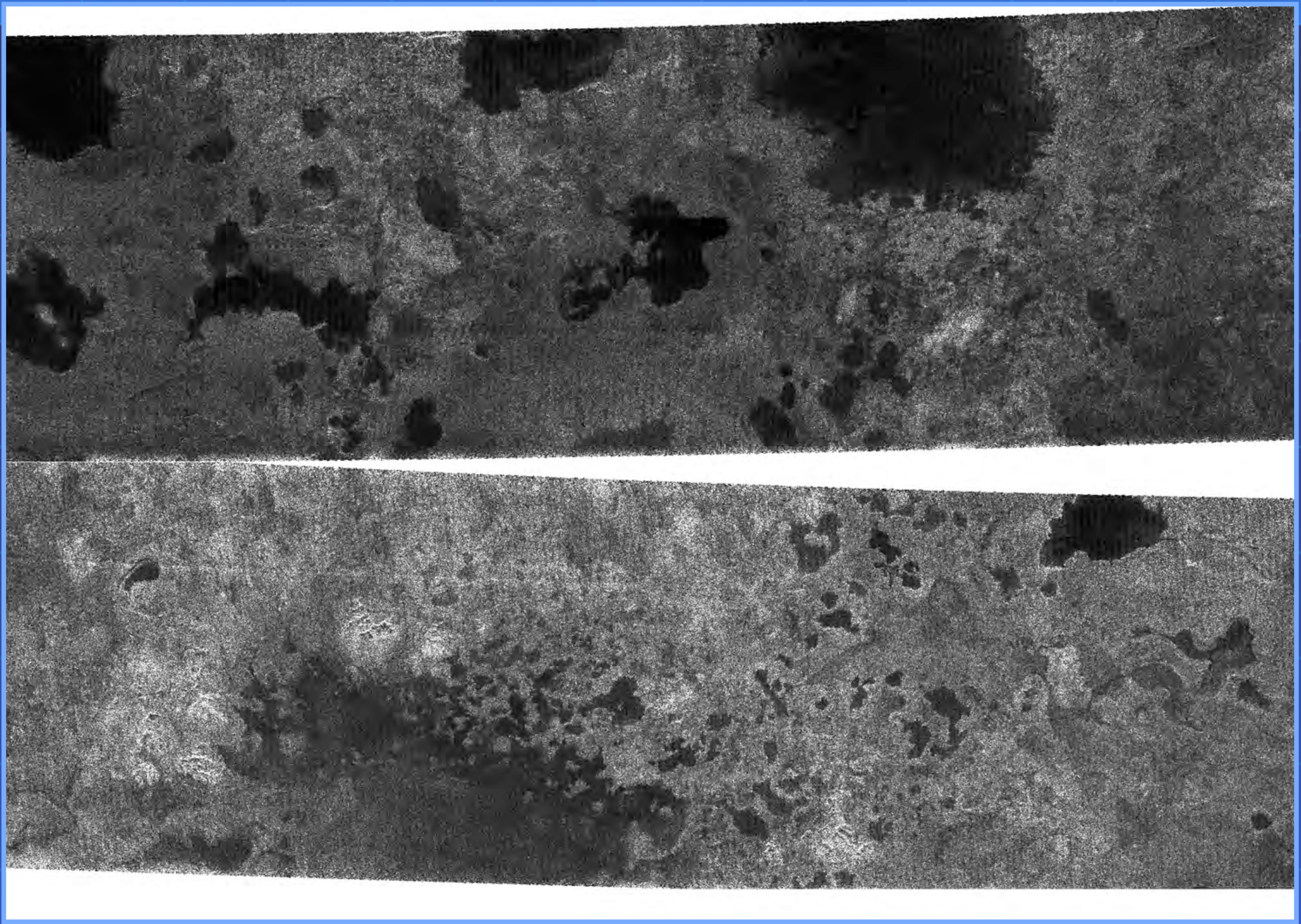


A Model of Titan's Interior

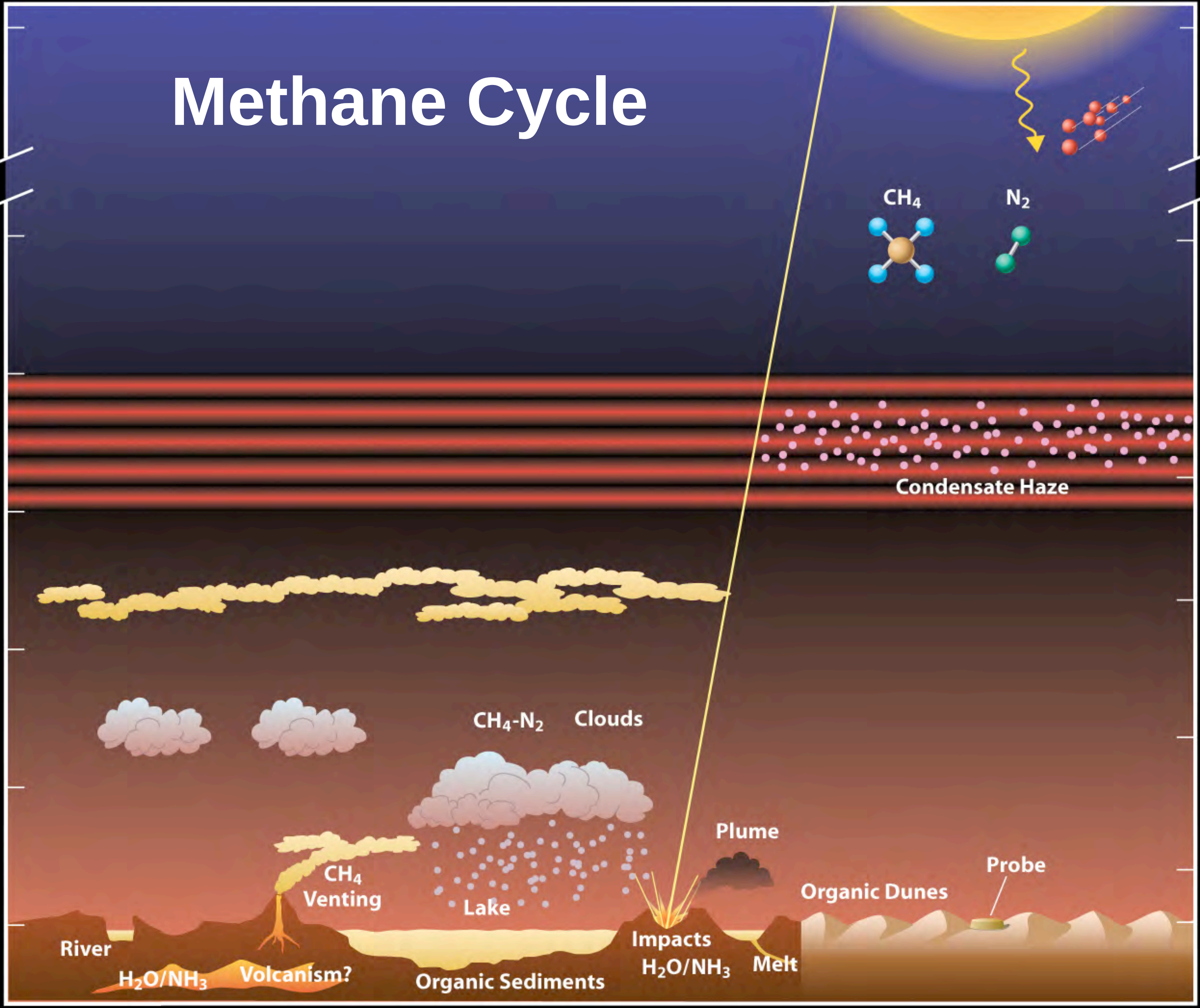
Cryo Volcanism

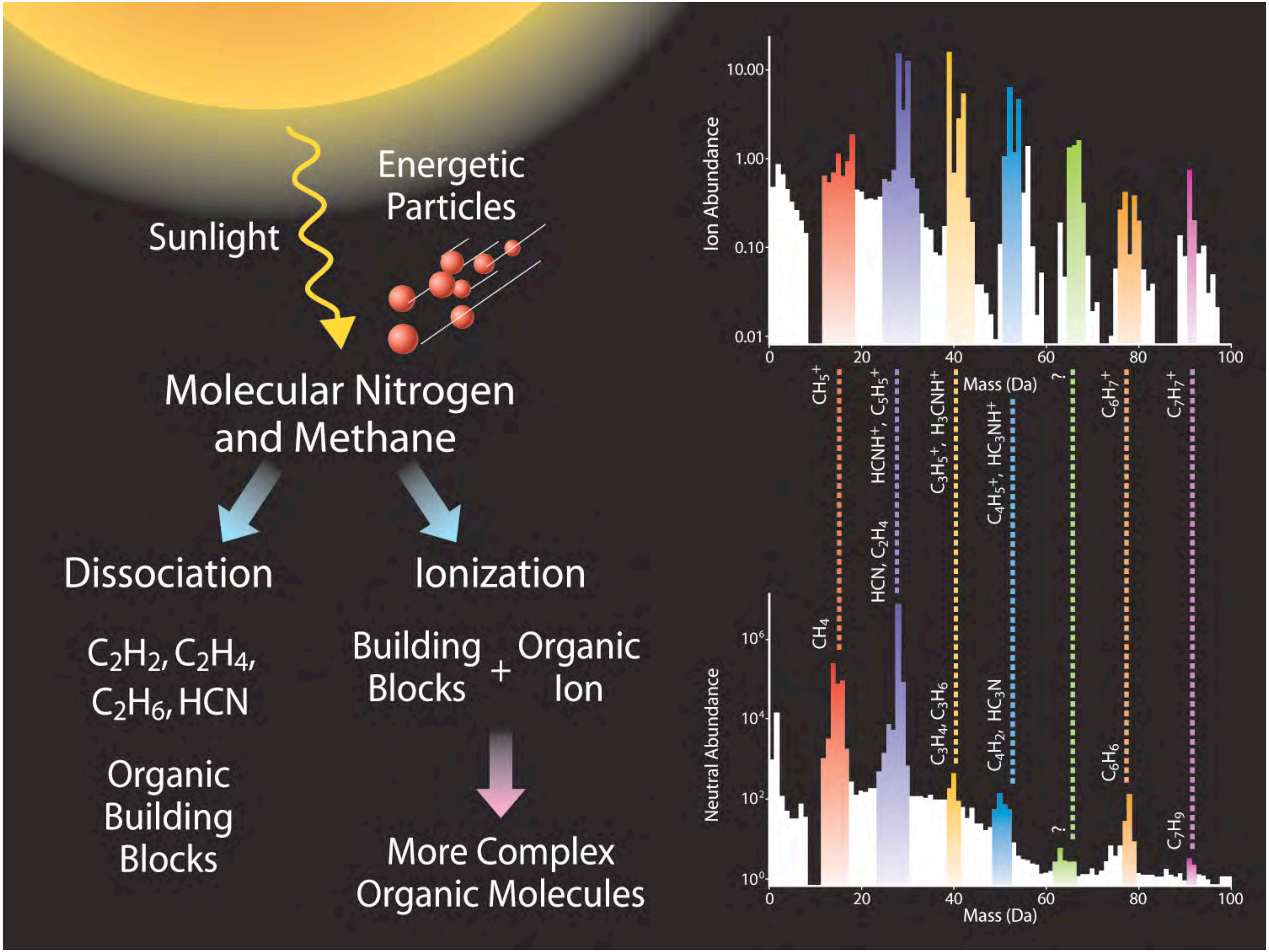


High Latitude Lakes



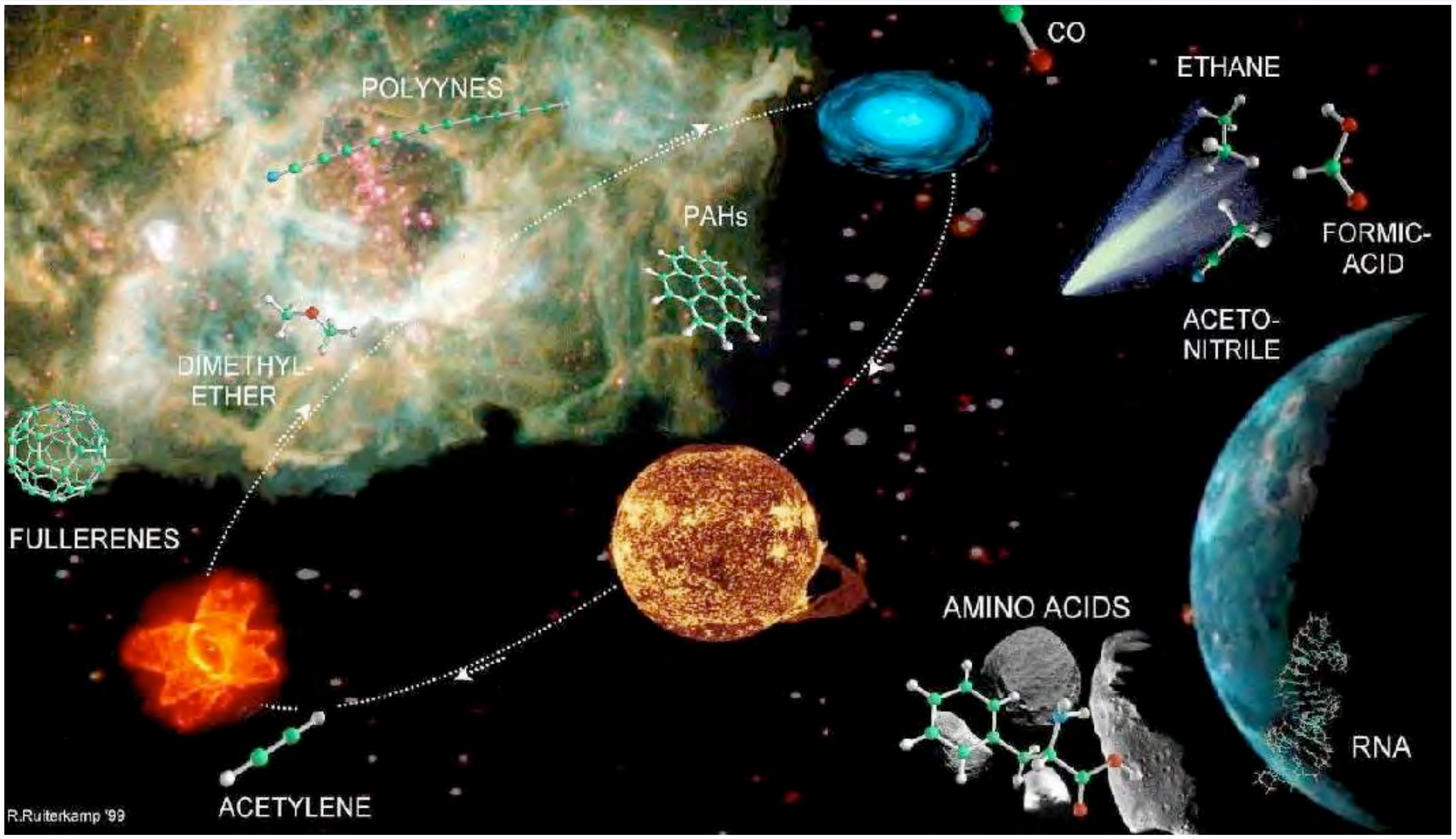
Methane Cycle





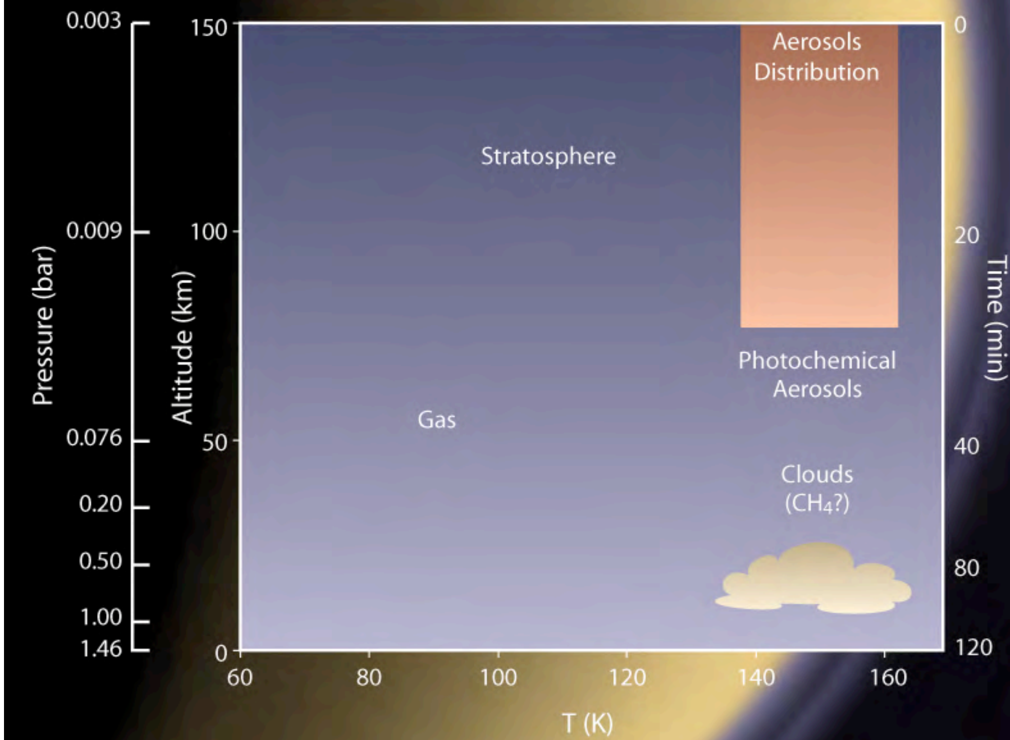
Sunlight
Energetic Particles
Molecular Nitrogen and Methane
Dissociation
Ionization
C2H2, C2H4, C2H6, HCN
Organic Building Blocks
Building Blocks + Organic Ion
More Complex Organic Molecules
Ion Abundance
10.00
1.00
0.10
0.01
0
20
40
60
80
100
Mass (Da)
CH5+
HCNH+, C5H5+
C3H5+, H3CNH+
C4H5+, HC3NH+
?
C6H7+
C7H7+
CH4
HCN, C2H4
C3H4, C3H6
C4H2, HC3N
?
C6H6
C7H9
Neutral Abundance
10^6
10^4
10^2
10^0
0
20
40
60
80
100
Mass (Da)

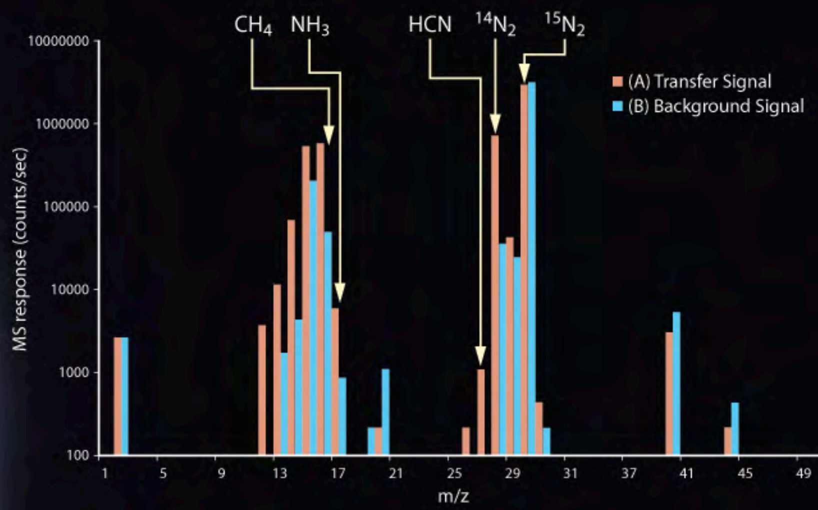
Interstellar Clouds

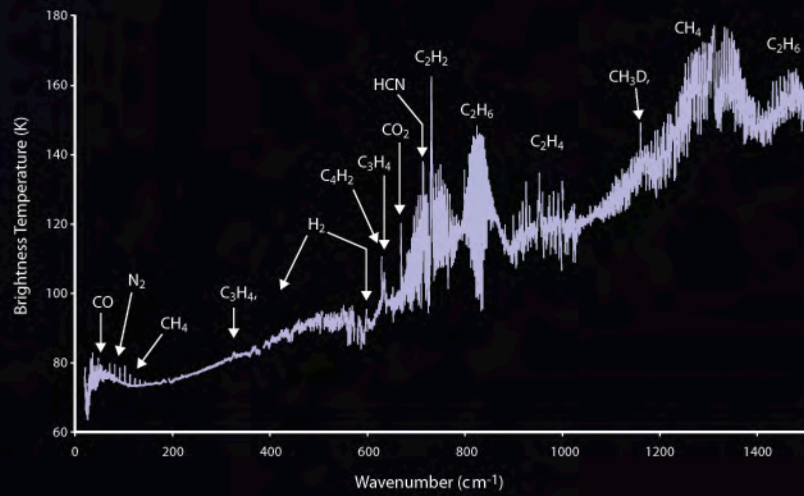


Organic Molecules in the Interstellar Medium, Comets and Meteorites: A Voyage from Dark Clouds to the Early Earth, Pascale Ehrenfreund & Steven B. Charnley, Annual Review of Astronomy & Astrophysics, 38:427-83, 2000

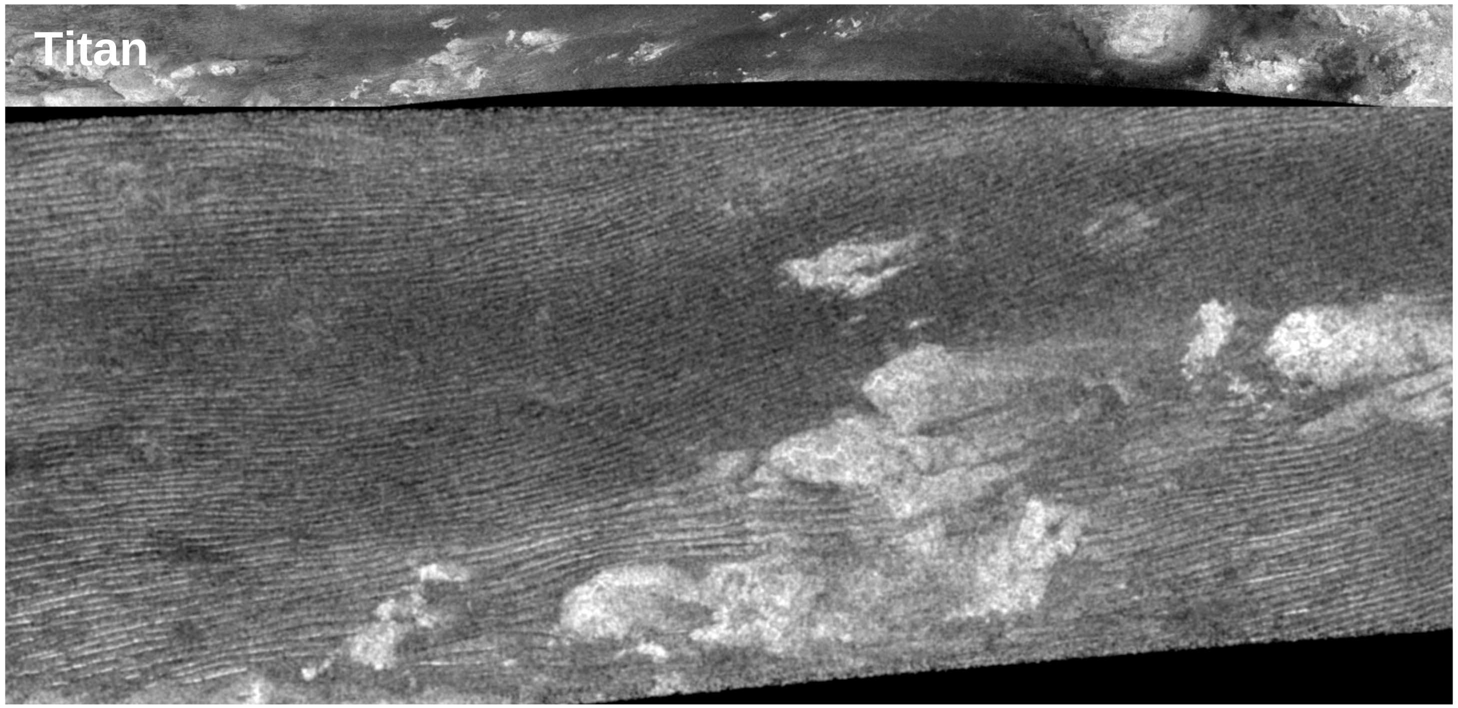
Stratospheric Composition



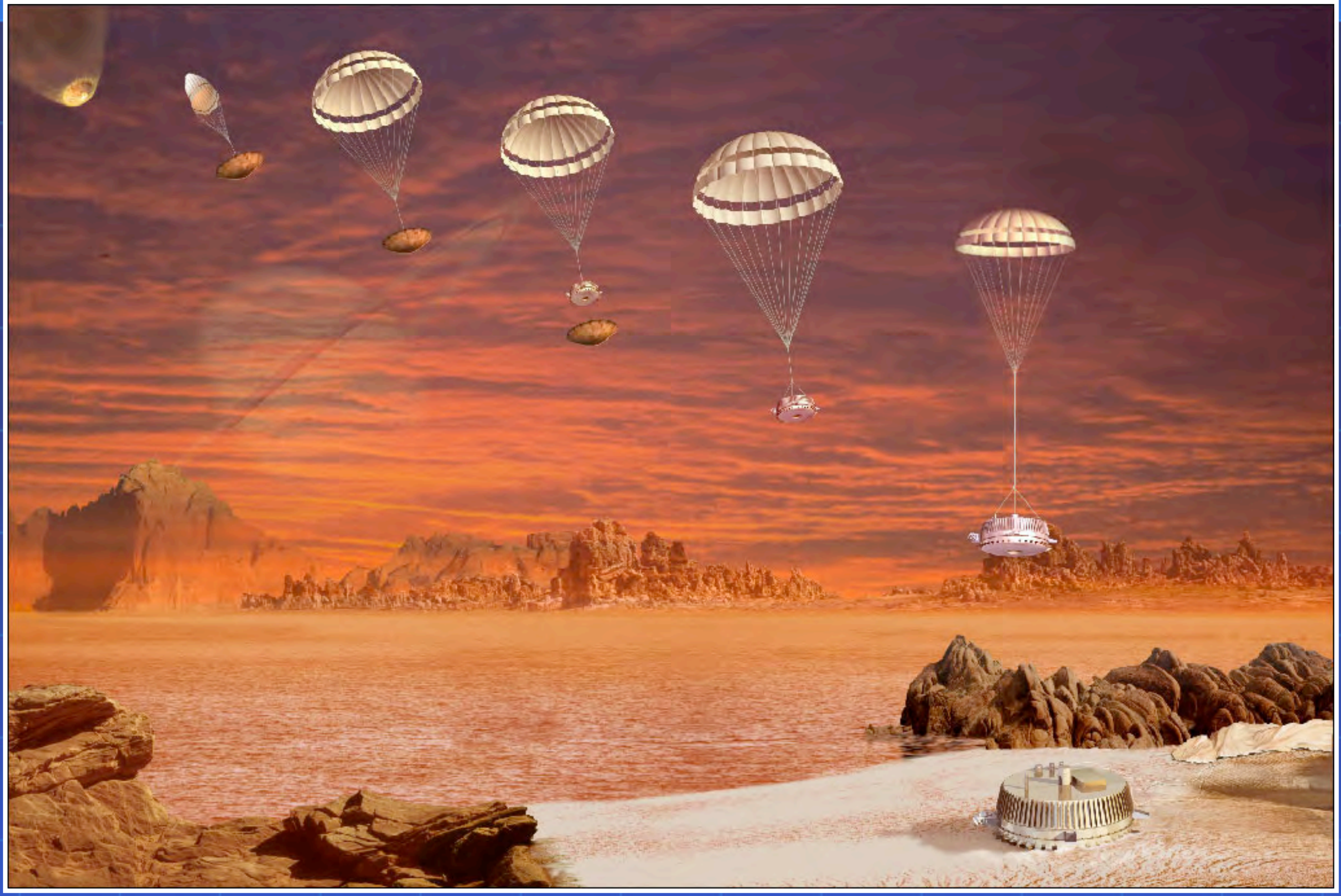


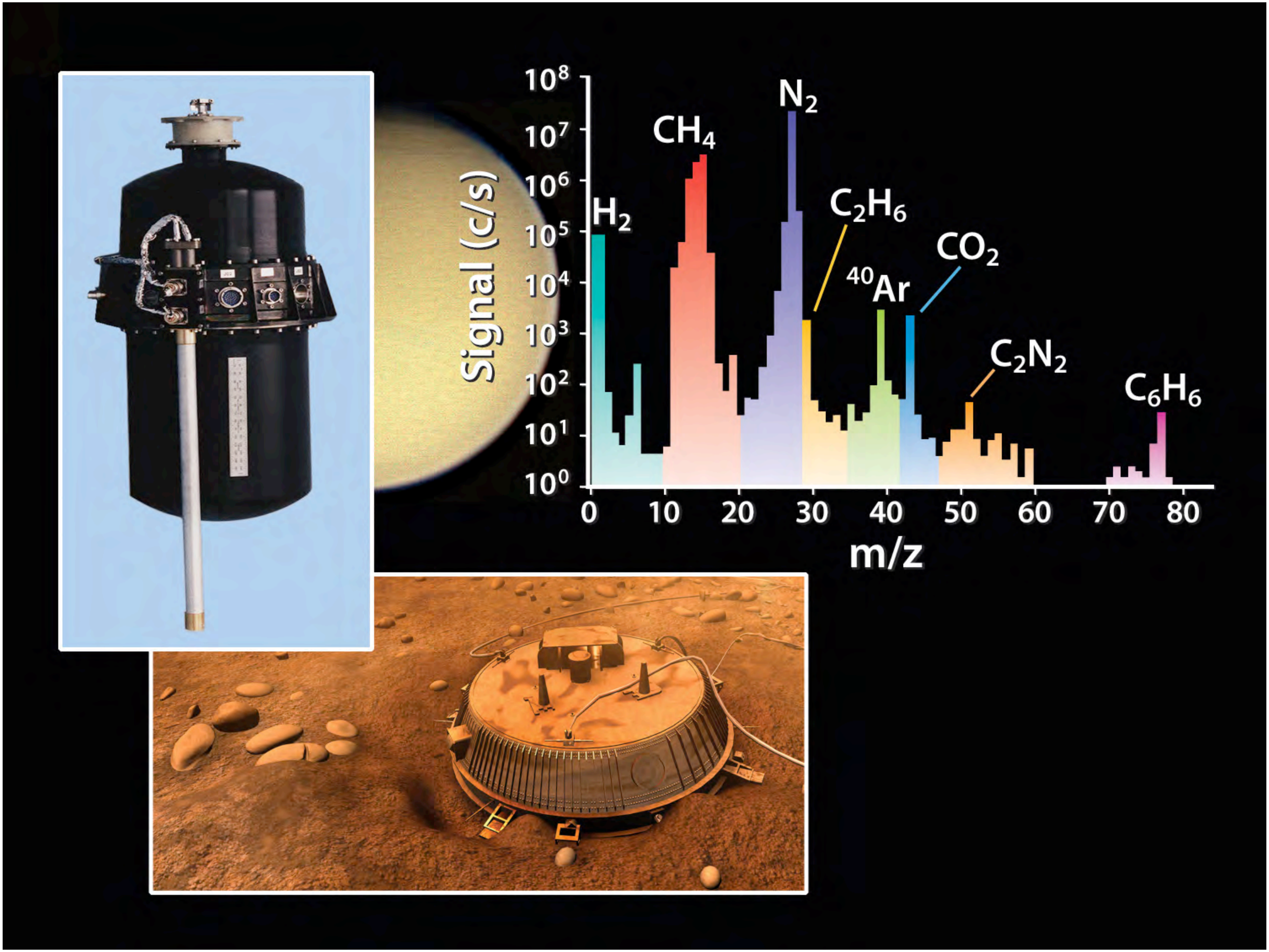


Dunes

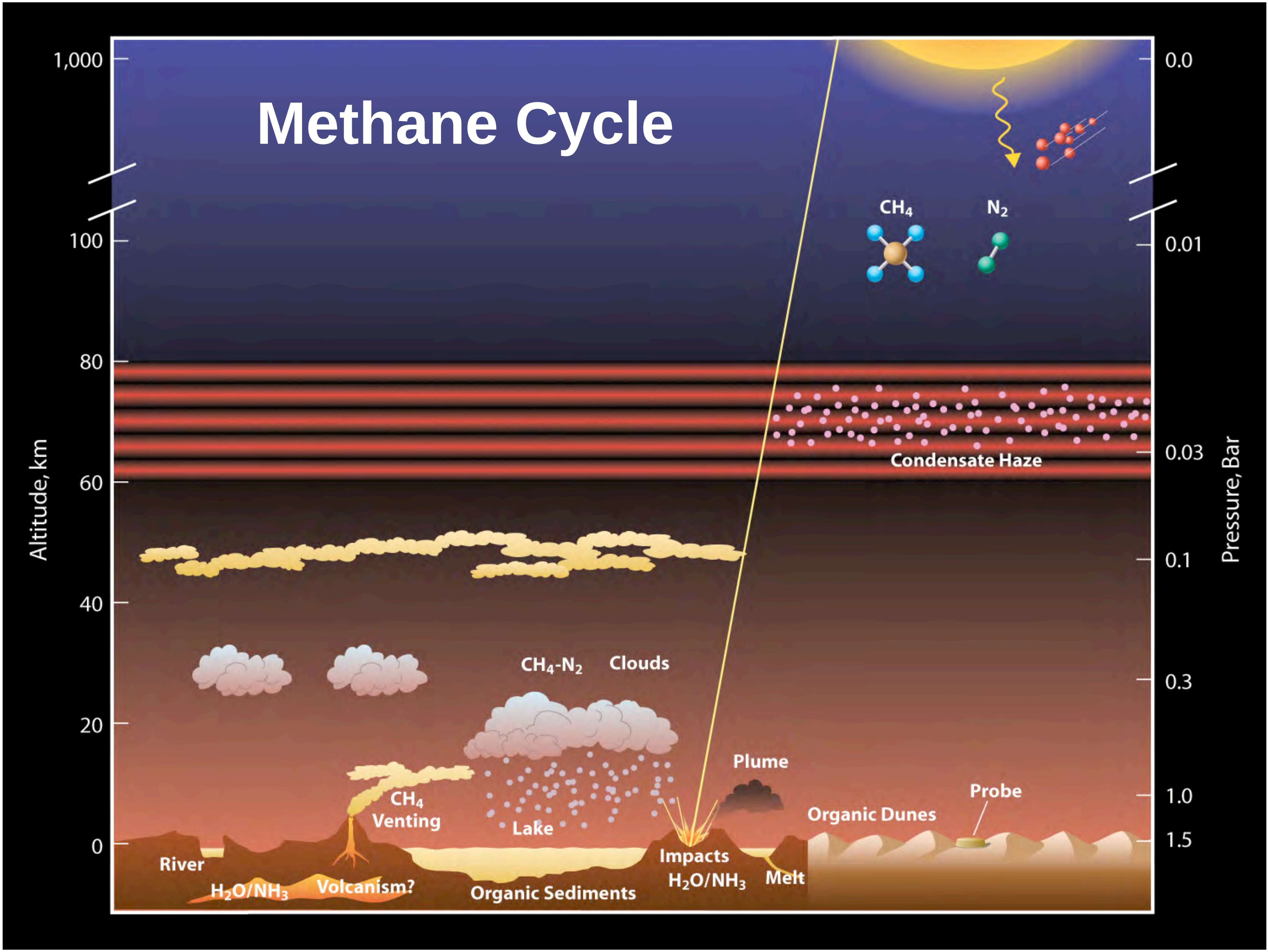


Descent Sequence





Signal (c/s)
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
H_2
CH_4
N_2
C_2H_6
^{40}Ar
CO_2
C_2N_2
C_6H_6
0 10 20 30 40 50 60 70 80
m/z

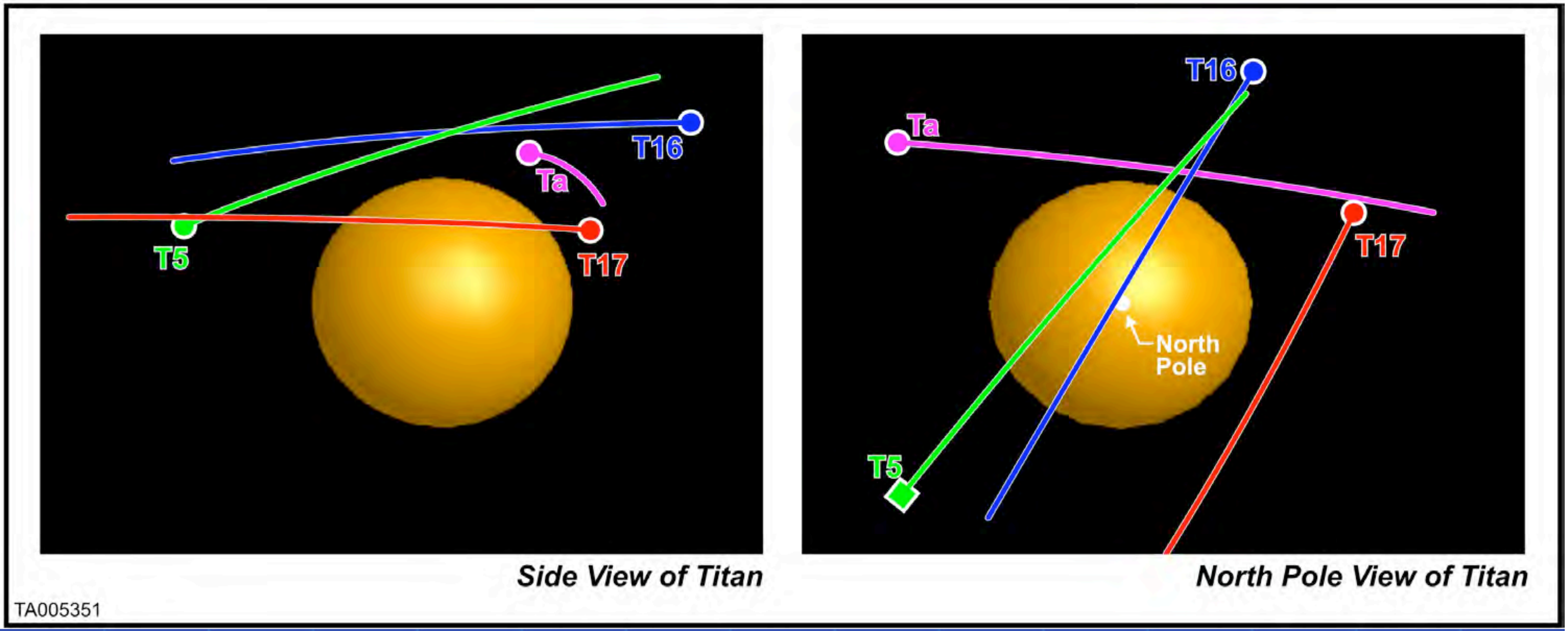


Methane Cycle
Altitude, km
1,000
100
80
60
40
20
0
Pressure, Bar
0.0
0.01
0.03
0.1
0.3
1.0
1.5
CH_4
N_2
Condensate Haze
CH_4-N_2 Clouds
Plume
CH_4 Venting
Lake
Probe
Organic Dunes
River
Impacts
H_2O/NH_3
Melt
H_2O/NH_3
Volcanism?
Organic Sediments

Ion Neutral Mass Spectrometer

About the mission and the instrument

Geometry of the T_a, T_b and T_5 trajectories: with respect to Titan



The Ion Neutral Mass Spectrometer

The 2 INMS sources

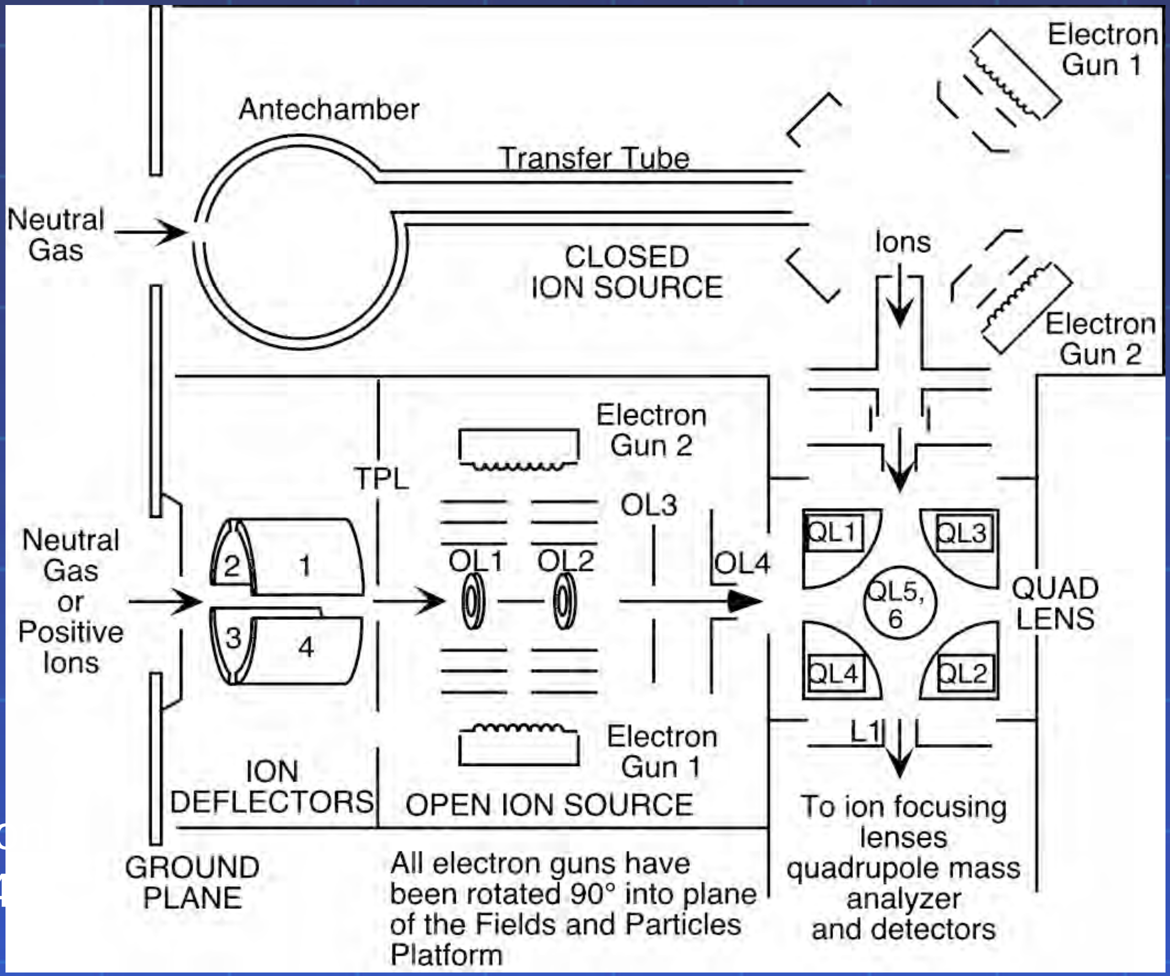
In this presentation:

- Neutral densities from closed source

- Ion densities from open source

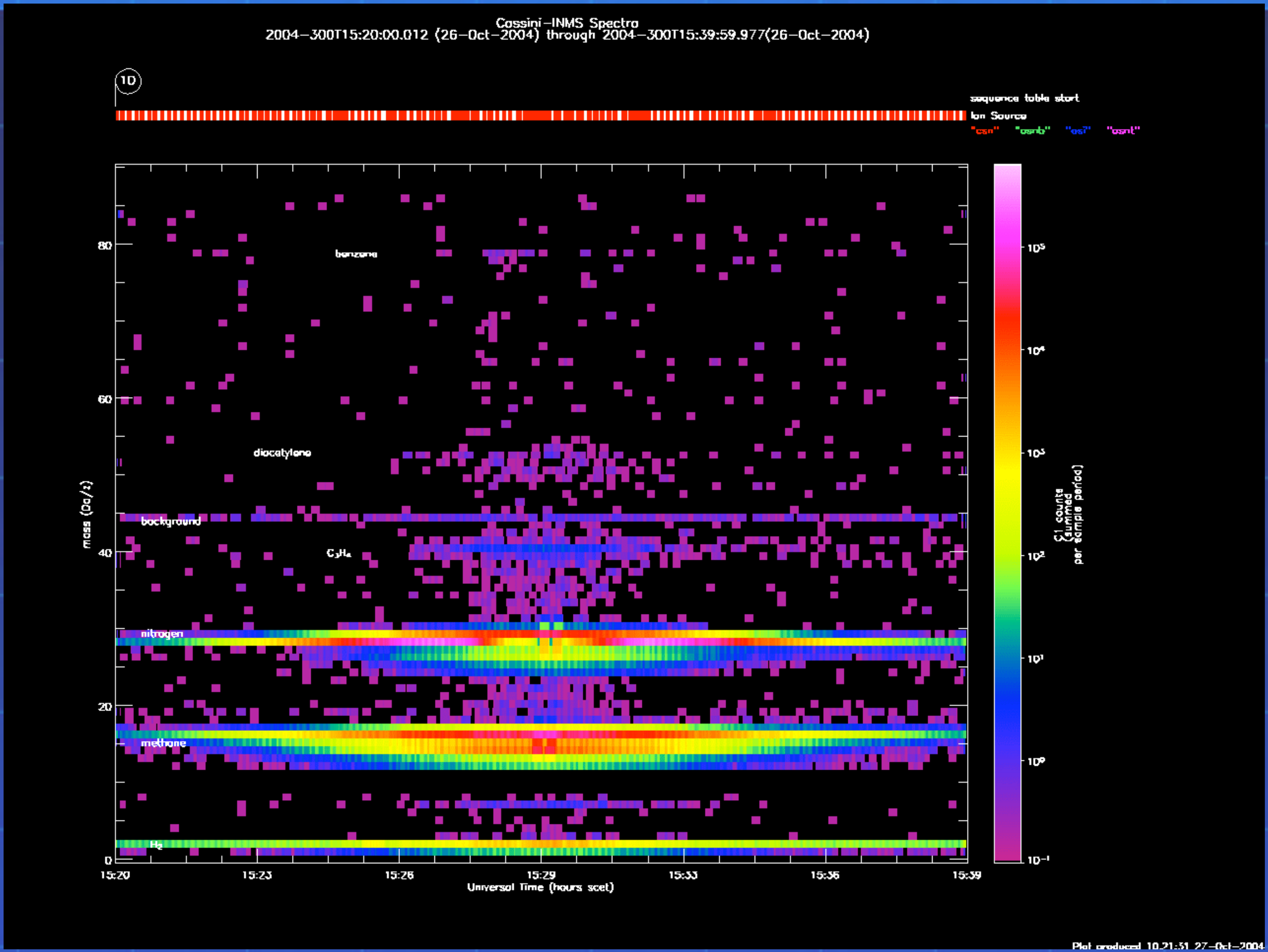
Note:

A molecule of N_2 penetrating inside the closed source can be ionized and dissociated into N_2^+ and N^+ and be observed in the detector o mass channels 28 and 14



Atmospheric Structure

Mass Spectrum recorded during T_a



N_2 →

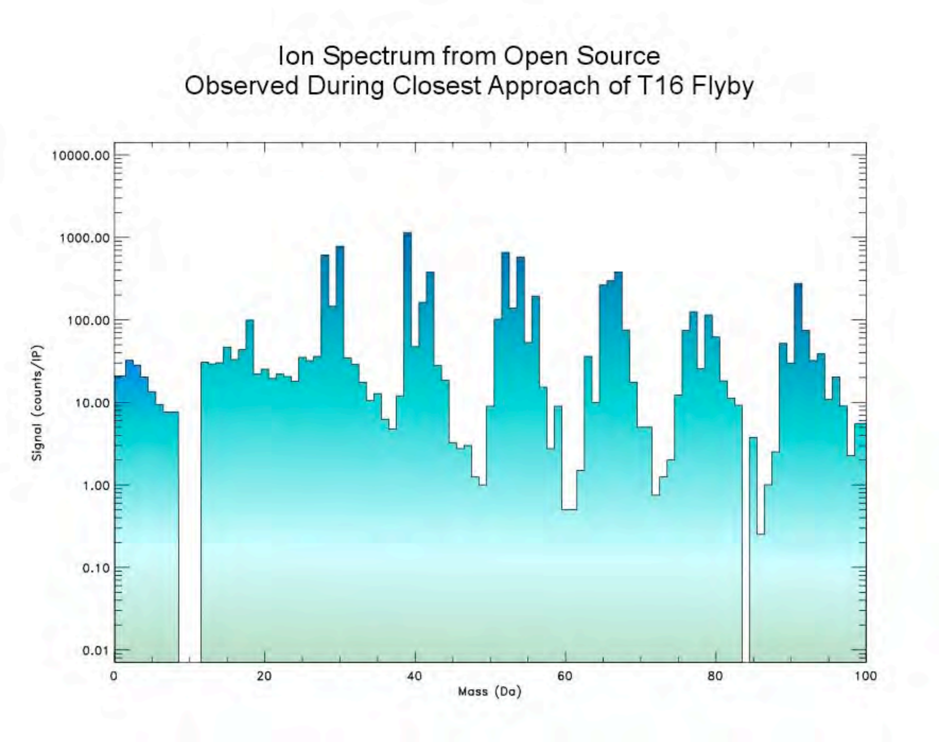
CH_4 →

H_2 →

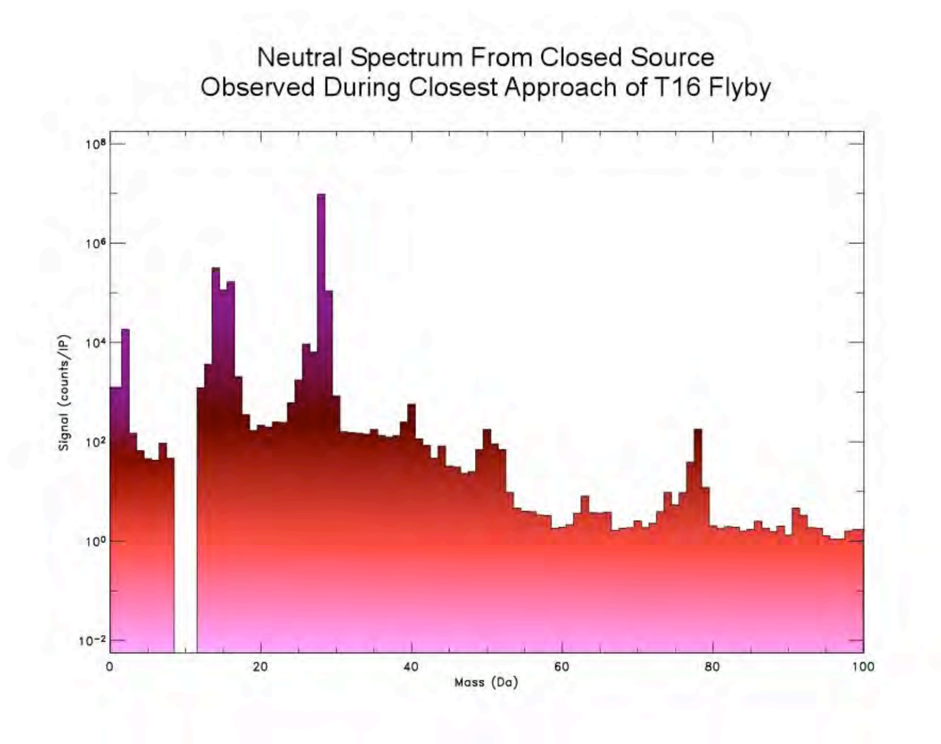
The Ion Neutral Mass Spectrometer

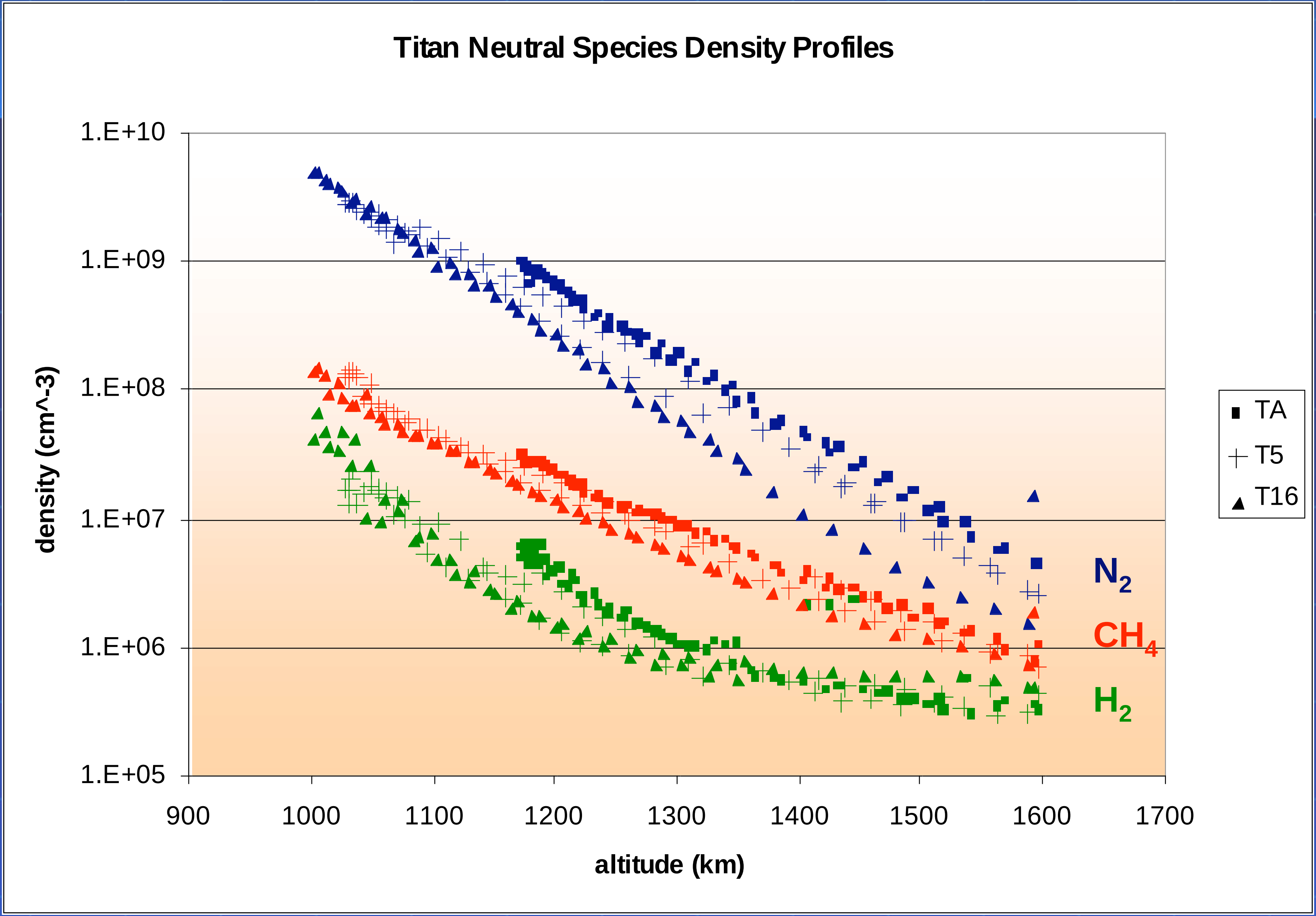
produces ion and neutral mass spectra

Ions

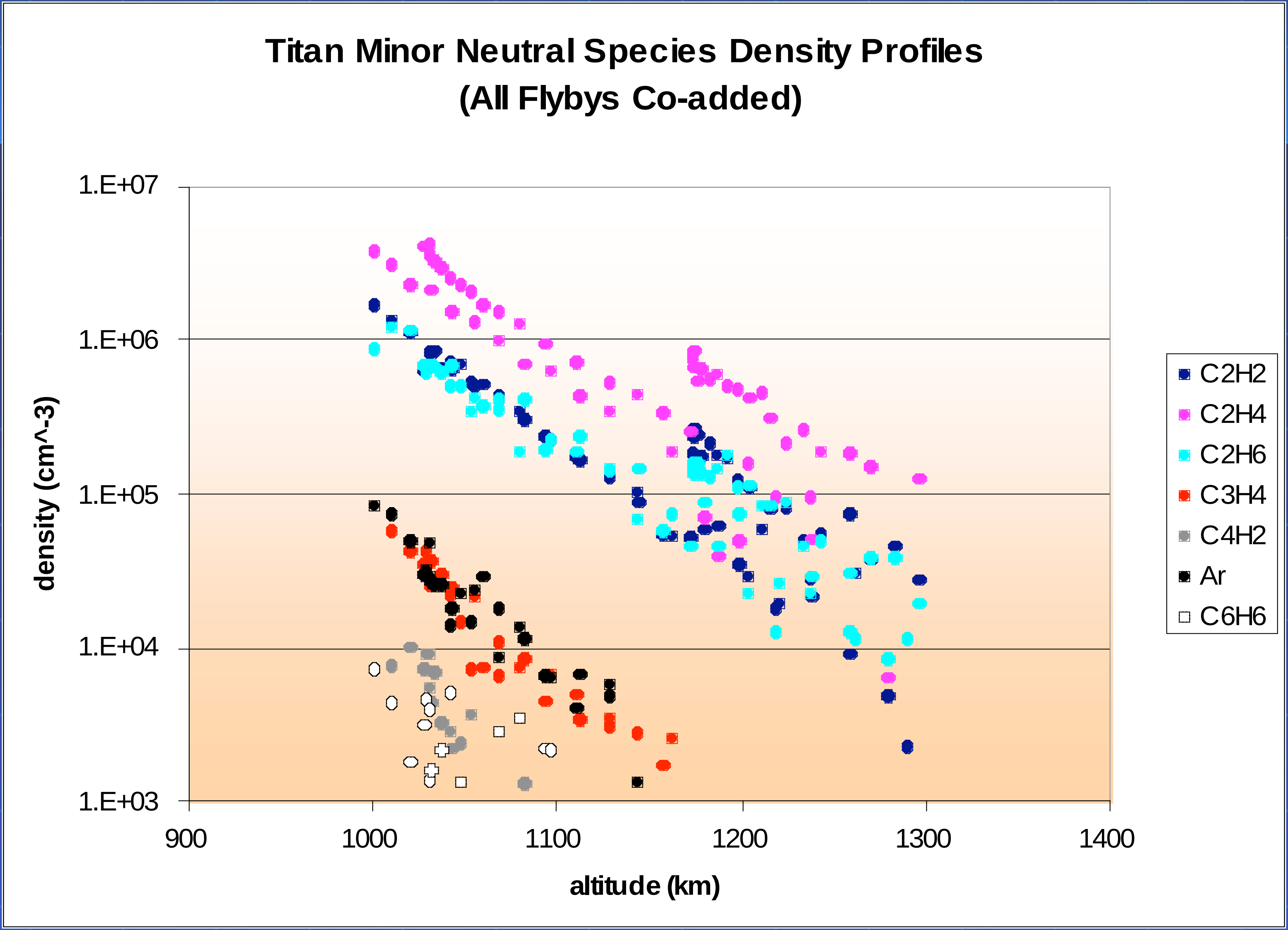


Neutral Gases





Titan Neutral Species Density Profiles
density (cm^-3)
1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
altitude (km)
900
1000
1100
1200
1300
1400
1500
1600
1700
TA
T5
T16
N2
CH4
H2



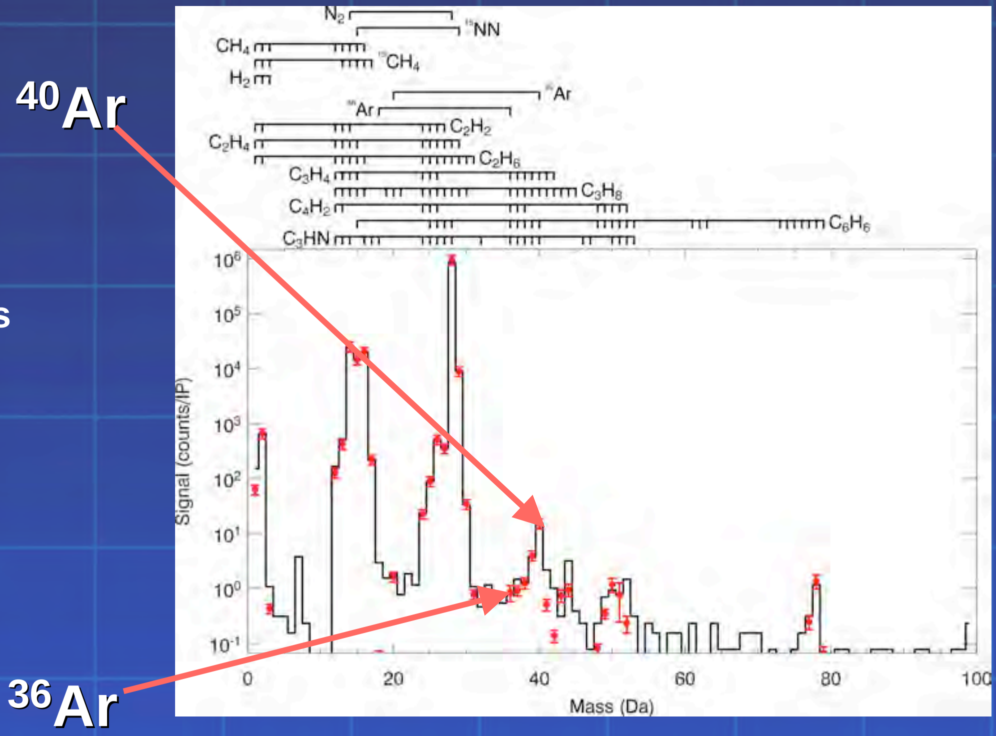
Titan Minor Neutral Species Density Profiles
(All Flybys Co-added)
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
density (cm^-3)
900
1000
1100
1200
1300
1400
altitude (km)
C2H2
C2H4
C2H6
C3H4
C4H2
Ar
C6H6

Relevance of INMS Observations

- Evolution of the atmosphere of Titan
  - Outgassing of the interior
  - Escape of gases from Titan
- Production of organic compounds
  - Ion and neutral photochemsitry
  - The role of the magnetospheric interacation

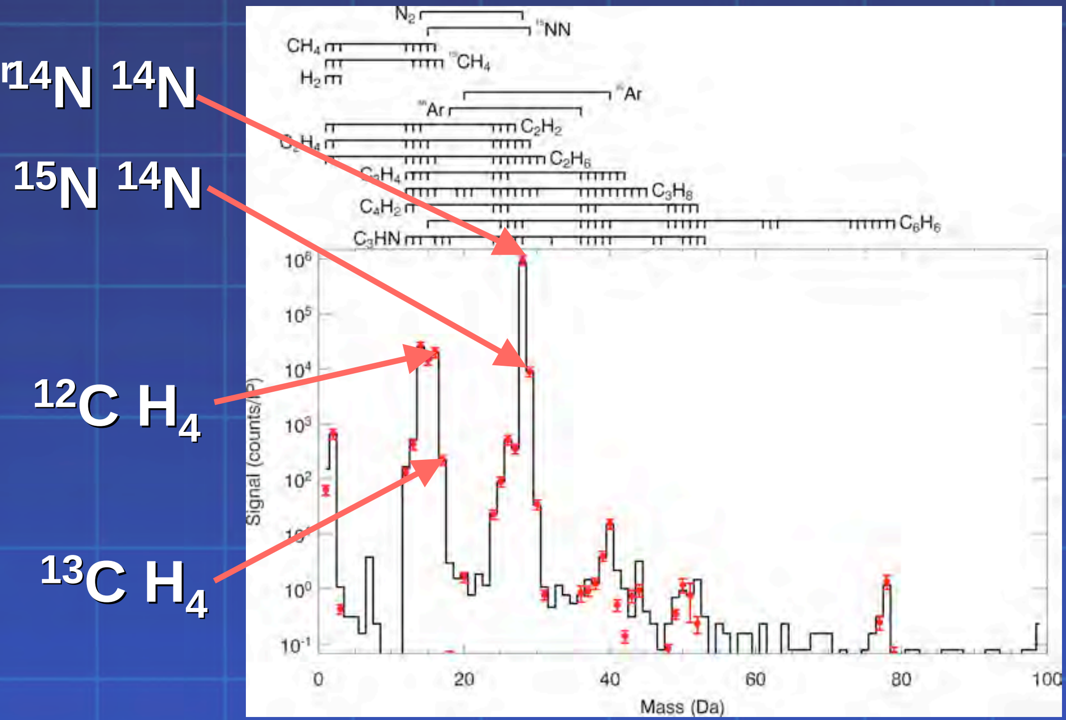
Evolution of the Atmosphere: Outgassing of the Interior

- **The isotopes of Argon tell us about outgassing from the interior**
  - **^{40}Ar tells us how much of the volatile material has been outgassed from the interior**
    - **^{40}Ar = 0.8 ppm --> ~2% of interior volatiles are outgassed**
  - **^{36}Ar tells us how volatile materials like molecular nitrogen and methane were formed**
    - **^{36}Ar < 0.6 ppm --> most nitrogen is derived from ammonia**



Evolution of the Atmosphere: Atmospheric Escape

- The isotopes of molecular nitrogen and methane tell us about escape of volatiles from the atmosphere
  - The ratio of ^{14}N to ^{15}N in molecular nitrogen tells us how much of the atmosphere has escaped over geological time
  - The ratio of ^{12}C to ^{13}C in methane tells us about escape of methane and isotopic fractionation from photodissociation of methane

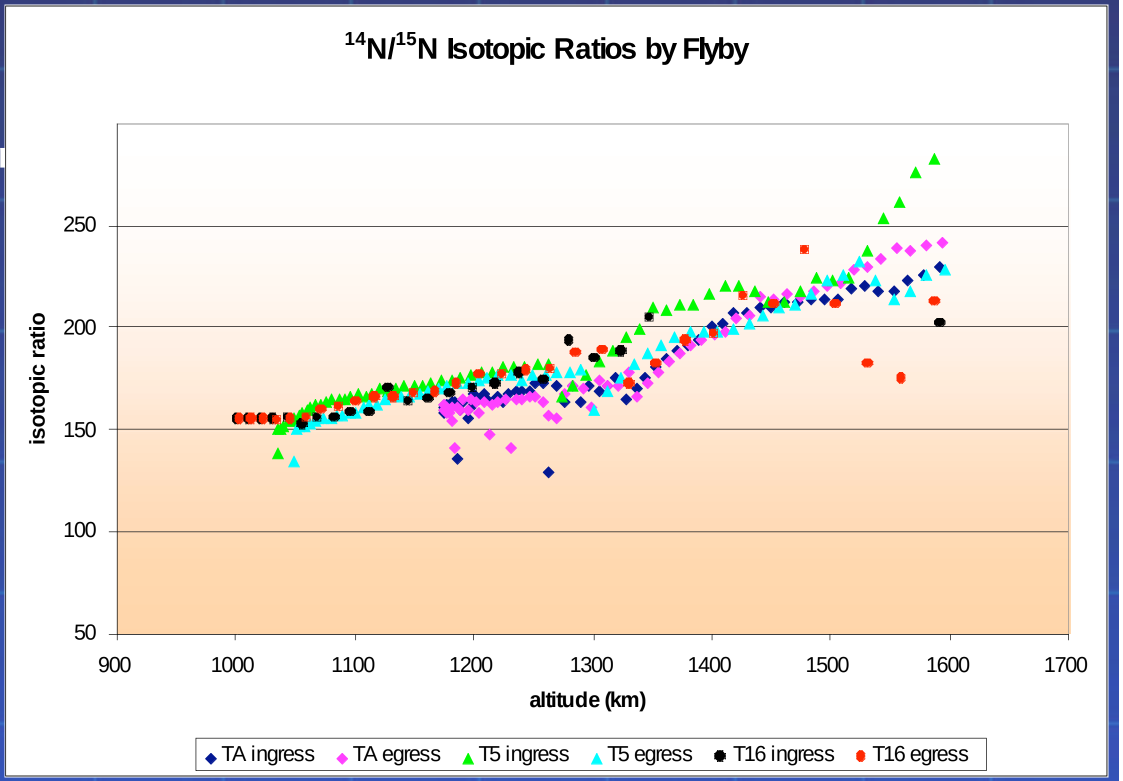


Evolution of the Atmosphere: Atmospheric Escape

- The isotopes of molecular nitrogen tell us about escape of nitrogen

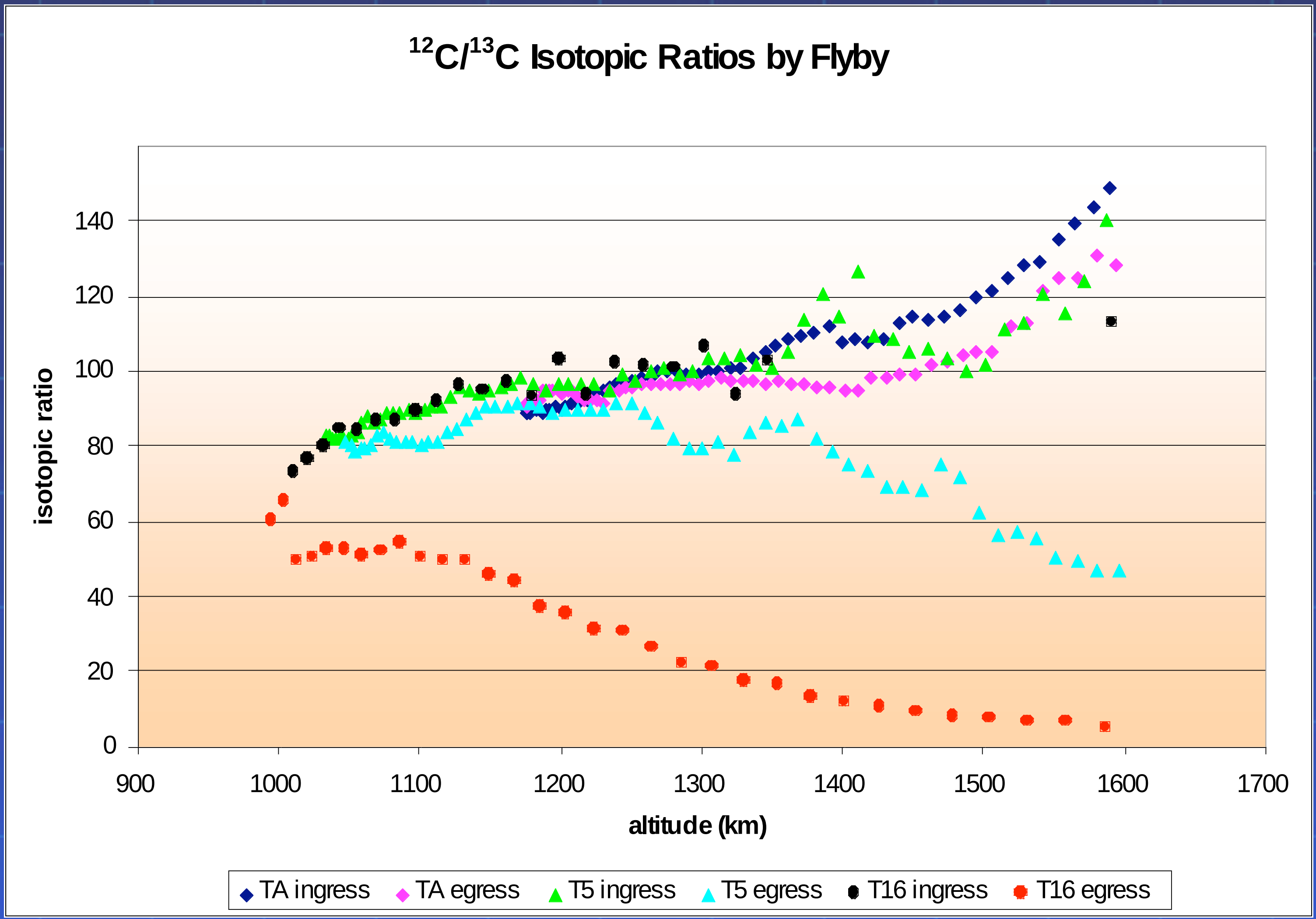
  – The ratio of ^{14}N to ^{15}N in molecular nitrogen tells us how much of the atmosphere has escaped over geological time

300 – The change in the ratio as a function of altitude is due to diffusive separation in the presence of gravity



Evolution of the Atmosphere: Atmospheric Escape

- **Methane isotopic ratios give us complimentary information**



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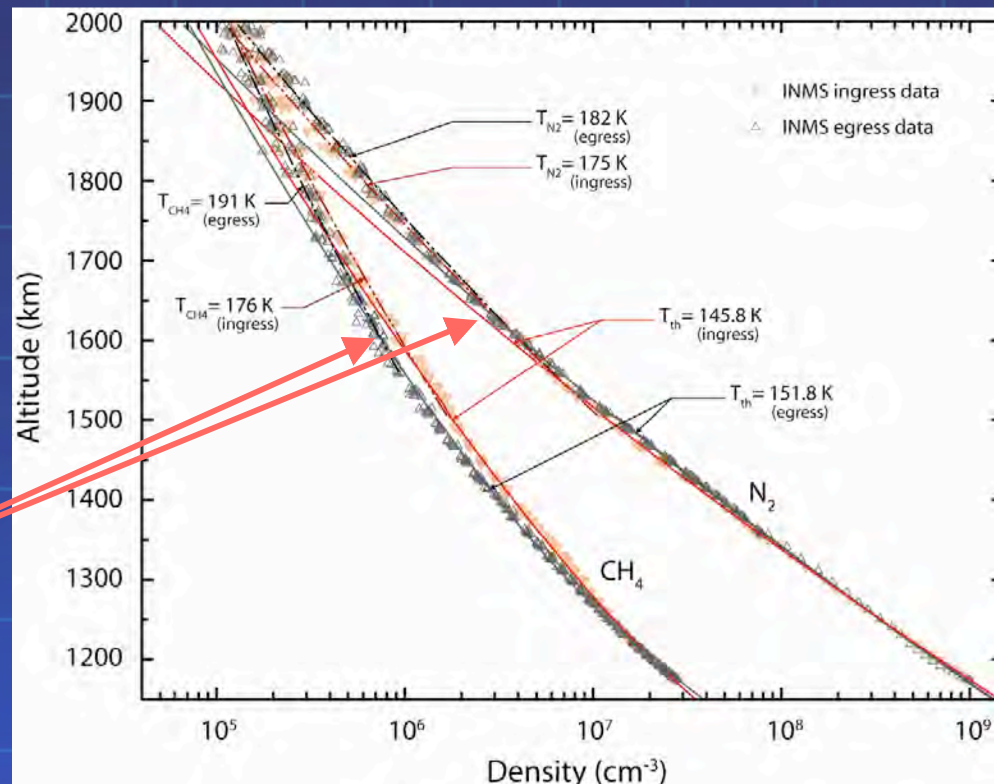
Evolution of the Atmosphere: Atmospheric Escape

- **INMS also sees direct evidence of heating of the upper atmosphere of Titan by energetic particles from Saturn's magnetosphere**

Divergence between the thermal exospheric profiles and the INMS data (z>1600 km)



Evolution of the Atmosphere: Atmospheric Escape

- **And these elevated coronal temperatures imply escape of nitrogen and methane**

Table 6: Liouville fit results for the INMS T_A, T_B and T_5 exospheric data, using the kappa function as energy distribution at the exobase.

			Resulting Fit Parameters κ	T_0 (K)	χ^2	Parameters Characterizing the Suprathermal Population n^* (cm^{-3})	Φ_{esc} $(cm^{-2}s^{-1})$	E_D^* $(eV\,cm^{-3}s^{-1})$	Solar Input E_D^{ph} $(eV\,cm^{-3}s^{-1})$
N_2	T_A	*ingress*	14.8	138.0	5×10^{-4}	3.0×10^5	1.4×10^3	6.1×10^1	9.0×10^5
		egress	8.86	119.9	4×10^{-4}	1.4×10^5	1.3×10^5	4.7×10^1	”
	T_B	*egress*	18.7	172.3	3×10^{-3}	1.6×10^6	1.2×10^3	2.0×10^2	8.9×10^5
	T_5	*ingress*	*85.7*	*147.9*	4×10^{-3}	6.4×10^{-1}	2.8×10^{-5}	7.0×10^{-4}	8.9×10^5
		egress	7.78	115.5	2×10^{-3}	1.1×10^5	2.2×10^5	3.4×10^1	”
CH_4	T_A	*ingress*	8.74	134.2	5×10^{-4}	7.7×10^4	1.5×10^6	2.1×10^1	9.0×10^5
		egress	5.85	126.7	6×10^{-4}	7.0×10^4	1.3×10^7	2.6×10^1	”
	T_B	*egress*	97.8	210.5	5×10^{-3}	3.1×10^5	4.9×10^3	4.9×10^1	8.9×10^5
	T_5	*ingress*	*17.0*	*126.4*	5×10^{-4}	4.0×10^2	7.5×10^3	2.7×10^{-1}	8.9×10^5
		egress	4.26	118.8	5×10^{-4}	8.6×10^4	5.1×10^7	3.6×10^1	”

κ, T_0 Fit parameters characterizing the energy distribution at the exobase
χ^2 Parameter characterizing the quality of the fit
n^* Density of the suprathermal particles at the exobase (numerically)
Φ_{esc} Escape flux at the exobase (numerically)
E_D^* Suprathermal energy density in the exobase region, assumed to be 85 km-thick (numerically)
E_D^{ph} Energy brought by solar photons into the 85 km-thick exobase layer

Evolution of the Atmosphere: Atmospheric Escape

- But not enough escape (10^{-4}) to explain the implications of the measured isotopic ratio of molecular nitrogen

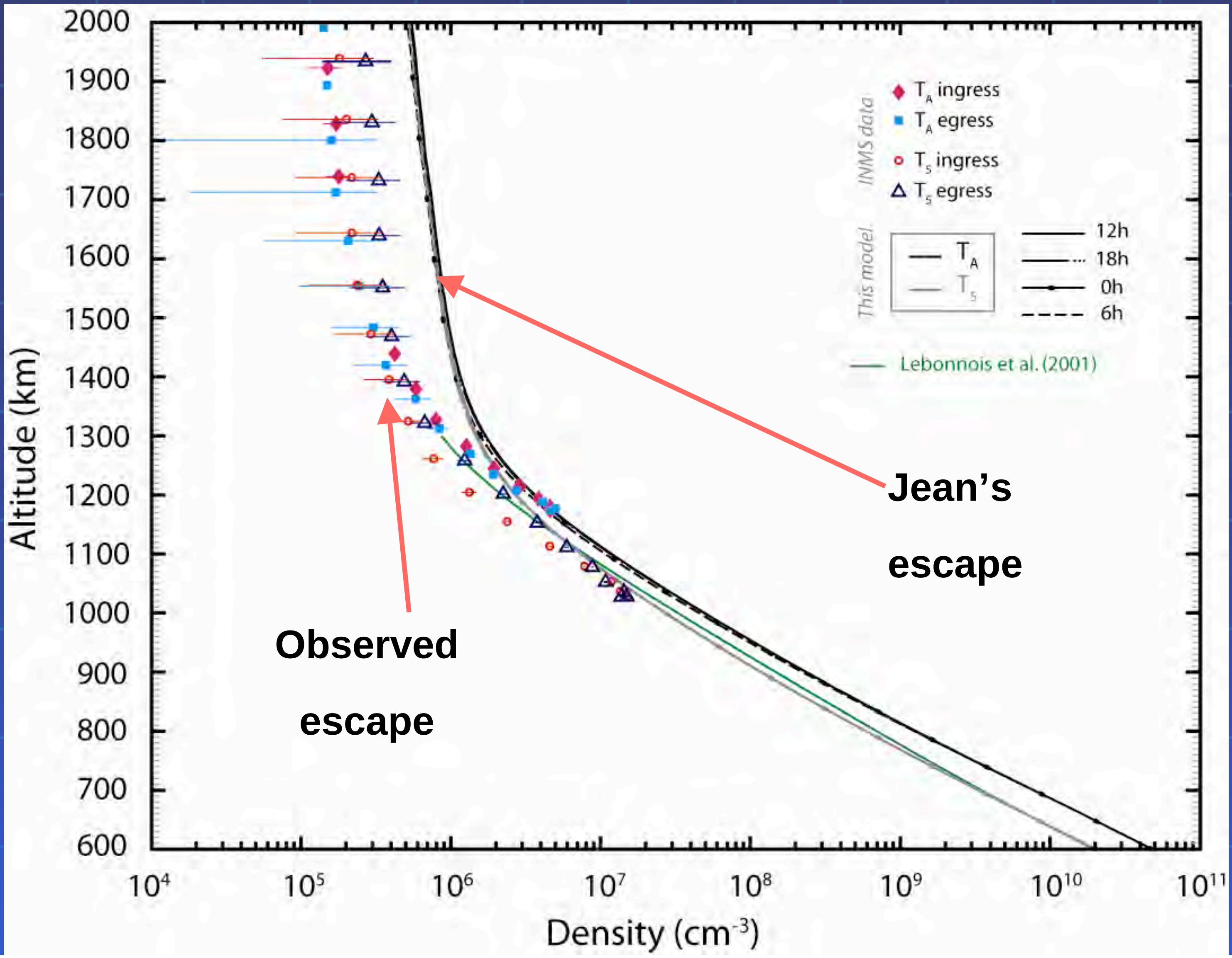
Isotopic Ratio	INMS value	Terrestrial Reference
$^{14}N/^{15}N$	155	215
$^{12}C/^{13}C$	96	93.8

- If we use the terrestrial $^{14}N/^{15}N$ as a reference this implies that over 70% of the Titan atmosphere has escaped over geological time, since the lighter isotope (^{14}N) escapes preferentially with regard to the heavier isotope, ^{15}N
- However, we note that in spite of the chemical loss of methane in the atmosphere and its escape from the atmosphere the value remains close to the terrestrial value implying resupply within the last 50 million years

Atmospheric Escape:

Molecular Hydrogen from Methane Conversion Escapes

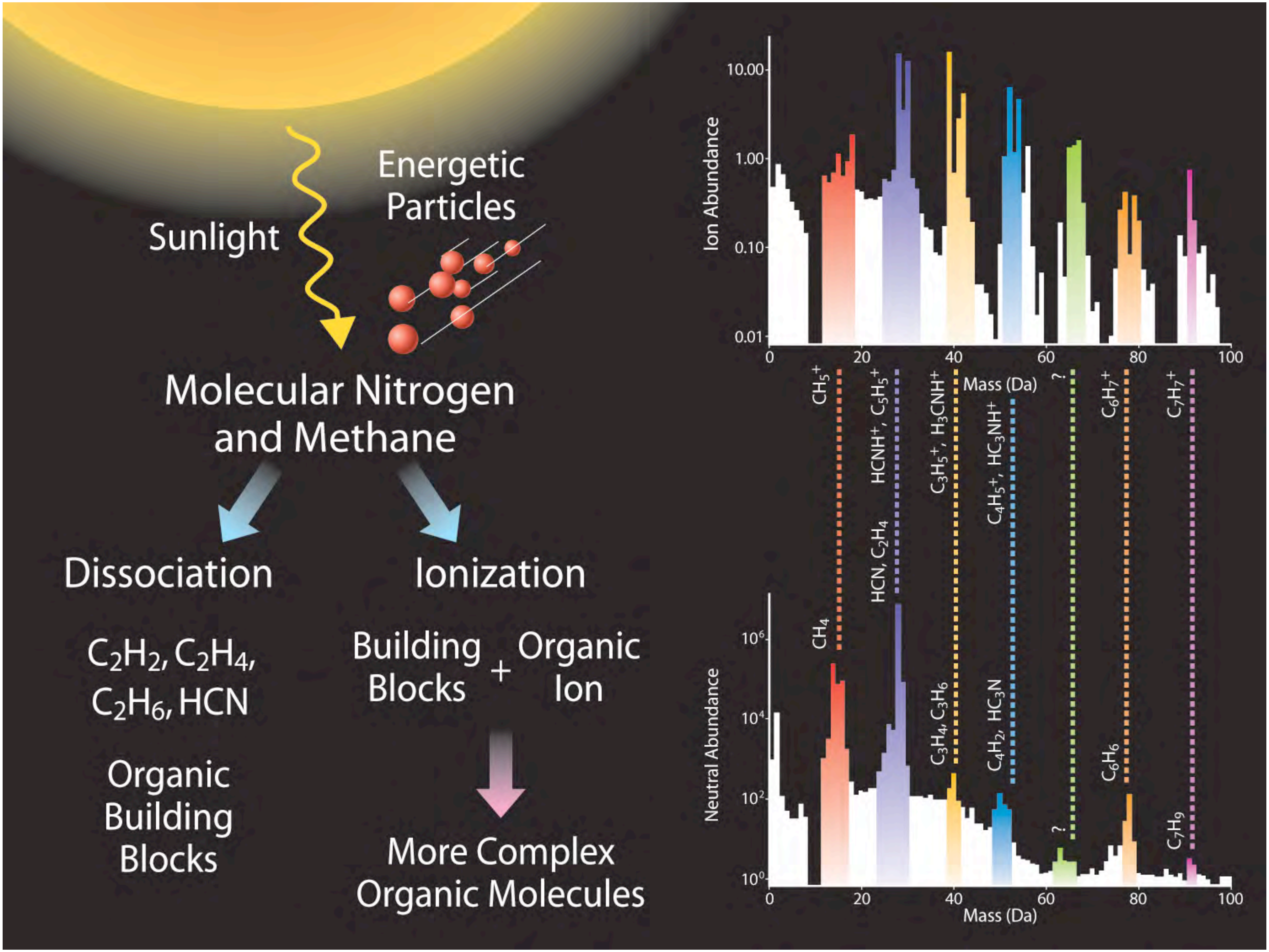
H_2 escapes three times faster than expected from Jean's escape



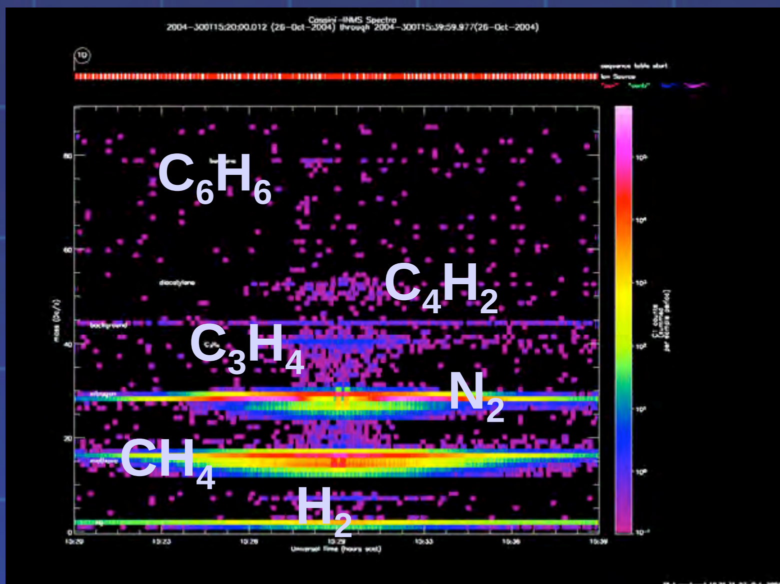
Ion Neutral Mass Spectrometer

Production of Complex Organics at High Altitude

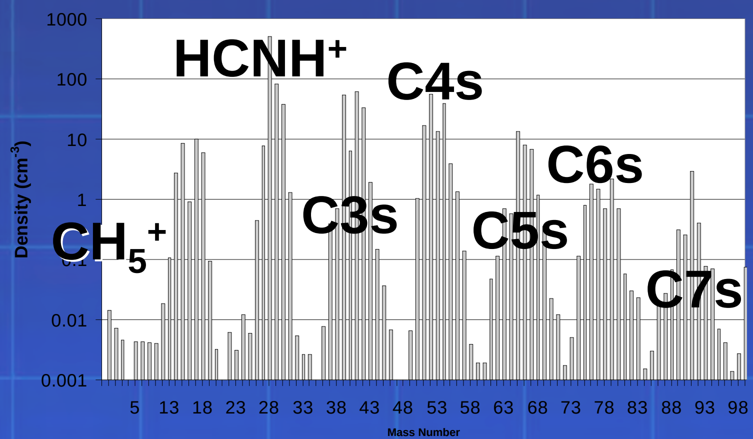
via Ion Neutral Chemistry


Sunlight
Energetic Particles
Molecular Nitrogen and Methane
Dissociation
Ionization
C_2H_2, C_2H_4, C_2H_6, HCN
Organic Building Blocks
Building Blocks + Organic Ion
More Complex Organic Molecules
Ion Abundance
10.00
1.00
0.10
0.01
0
20
40
60
80
100
Mass (Da)
CH_5^+
$HCNH^+$, $C_5H_5^+$
$C_3H_5^+$, H_3CNH^+
$C_4H_5^+$, HC_3NH^+
?
$C_6H_7^+$
$C_7H_7^+$
CH_4
HCN, C_2H_4
C_3H_4, C_3H_6
C_4H_2, HC_3N
?
C_6H_6
C_7H_9
Neutral Abundance
10^6
10^4
10^2
10^0
0
20
40
60
80
100
Mass (Da)

Complex Carbon Nitrile Chemistry



Average Mass
1100 - 1300 km



- The neutral composition at 1200 km in addition to the primary constituents N_2, CH_4, and H_2 includes a host of hydrocarbons: C_2H_2, C_2H_2, C_2H_6,C_3H_4, C_3H_8, C_4H_2, HCN, HC_3N, C_2N_2, and C_6H_6.

==> TITAN"S UPPER ATMOSPHERE IS A KEY SOURCE of CARBON NITRILE COMPOUNDS

- Correspondingly, the ionospheric composition has a complex hydrocarbon/nitrile chemistry that includes almost all possible hydrocarbon and nitrile species through C7.

IV.2 The Composition:

photo- and electron impact ionization and dissociations

- **Nitrogen**

$$N_2 + h\nu \rightarrow N(^4S) + N(^2D)$$
$$\rightarrow N_2^+$$
$$\rightarrow N^+ + N(^4S)$$

$$N_2 + e^- \rightarrow N(^4S) + N(^4S)$$
$$\rightarrow N(^2D) + N(^4S)$$
$$\rightarrow N(^2P) + N(^4S)$$
$$\rightarrow N(^2D) + N(^2D)$$
$$\rightarrow N_2^+$$
$$\rightarrow N^+ + N(^4S)$$
$$\rightarrow N^+ + N(^2D)$$

- **Methane**

Products	*Mordaunt et al.* (1993)		*Romani* (1996)	*Smith and Raulin* (1999)
	scheme 1	scheme 2		
$CH_3 + H$	0.51	0.49	0.41	0.41
$^3CH_2 + 2H$	0.25	0	0.21	0
$^1CH_2 + H_2$	0.24	0	0.28	0.53
$^1CH_2 + 2H$	0	0	0	0
$CH + H_2 + H$	0	0.51	0.10	0.06

- **Acetylene**

Products	Scheme 1			Scheme 2
	Okabe (1981, 1983) *Seki and Okabe* (1993)			*Vuitton and Yelle* (2005) *Läuter et al.* (2002)
	1470 Å	**1849 Å**	**1933 Å**	**1216 & 1933 Å**
$C_2H_2^{**}$	0.6	0.84	0.6	0
$C_2H + H$	0.3	0.06	0.3	$\simeq 1$
$C_2 + H_2$	≤ 0.1	≤ 0.1	≤ 0.1	0

- **Ethylene**

$$C_2H_4 + h\nu \rightarrow C_2H_2 + H_2$$
$$\rightarrow C_2H_2 + 2H$$

$C_2H_4^+, C_2H_3^+$,..., to H^+

- **Ethane**

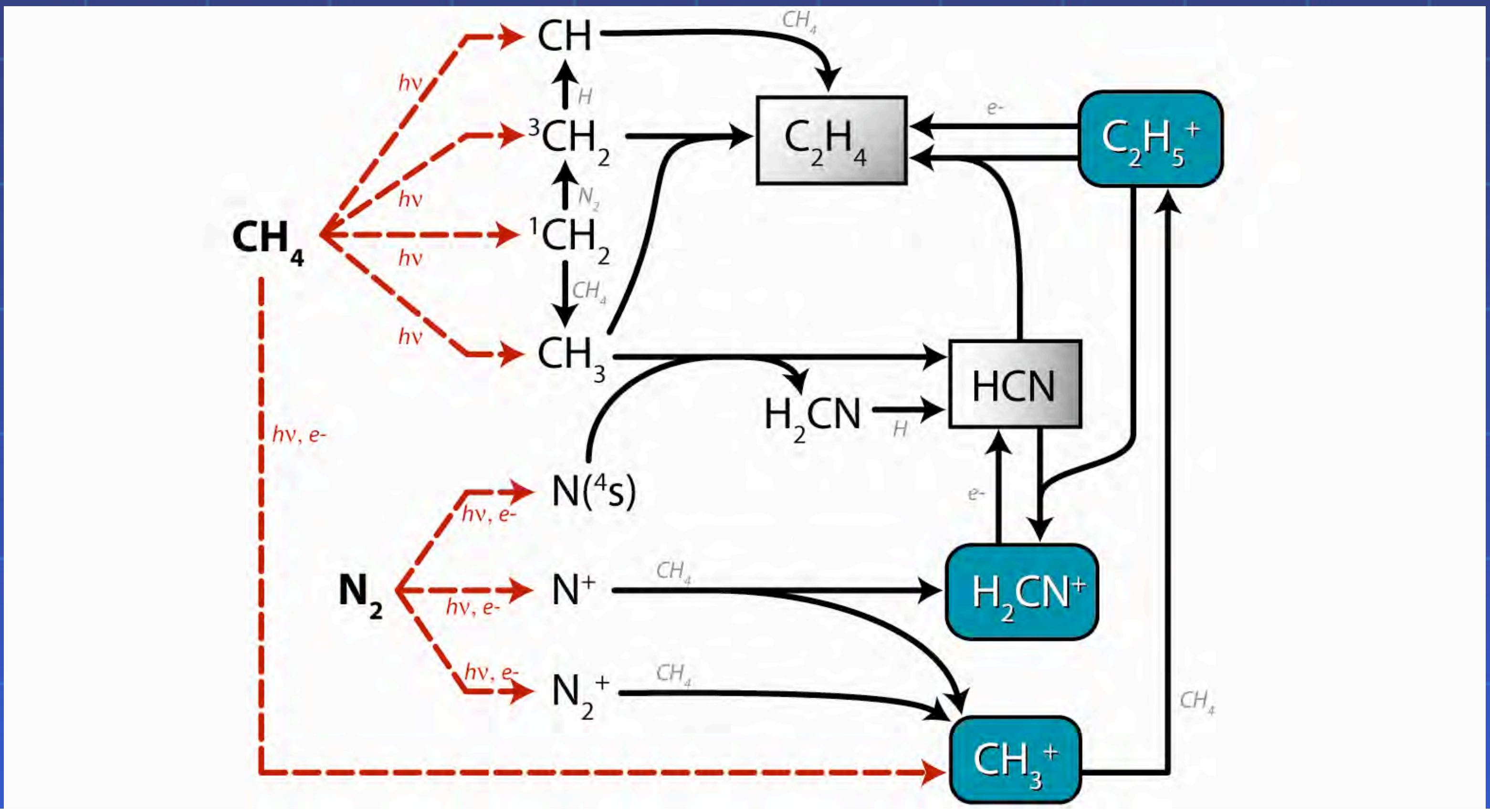
$$C_2H_6 + h\nu \rightarrow C_2H_4 + H_2,$$
$$\rightarrow C_2H_4 + 2H,$$
$$\rightarrow C_2H_2 + 2H_2,$$
$$\rightarrow CH_4 + {}^1CH_2,$$
$$\rightarrow 2CH_3,$$

$C_2H_6^+, C_2H_5^+$,..., to H^+

- **H, H_2, N, HCN, HC_3N, C_2N_2**

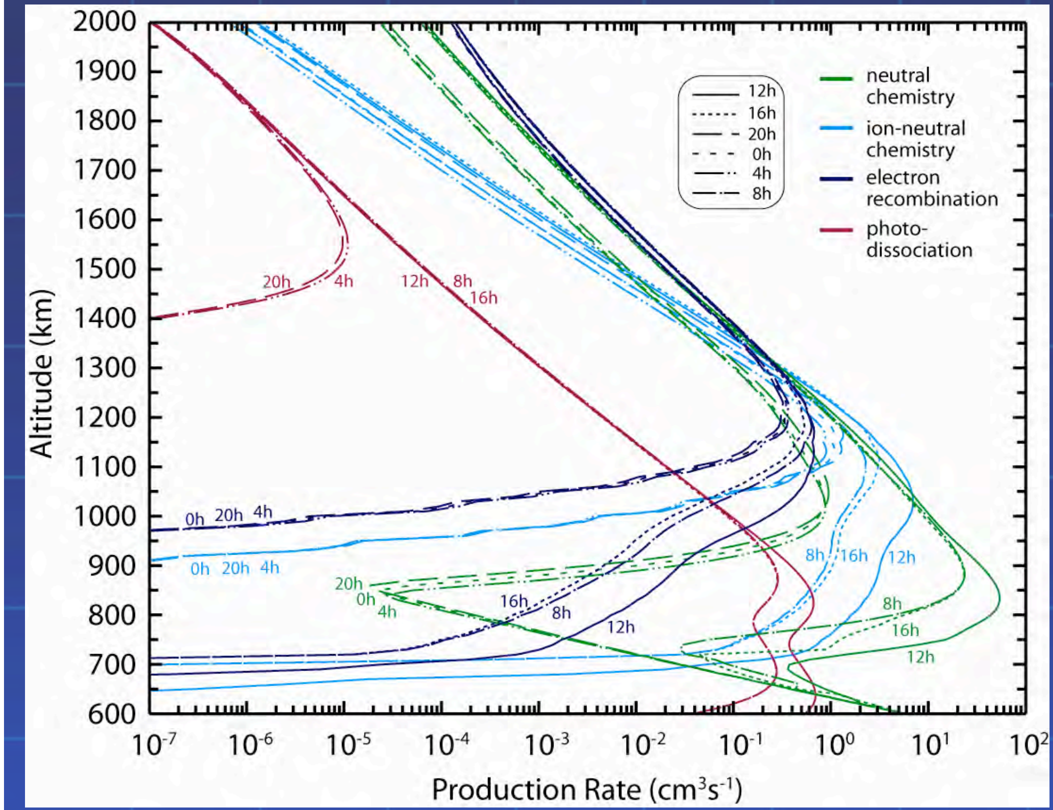
IV.3 The Composition:
the main ion-neutral scheme

- The chemical scheme starts from the photo- and electron impact dissociation and ionization of Nitrogen and Methane
  - **Creation of the first key neutrals: C_2H_4 and HCN**
  - **Production of the major ions: H_2CN^+, $C_2H_5^+$, CH_3^+**



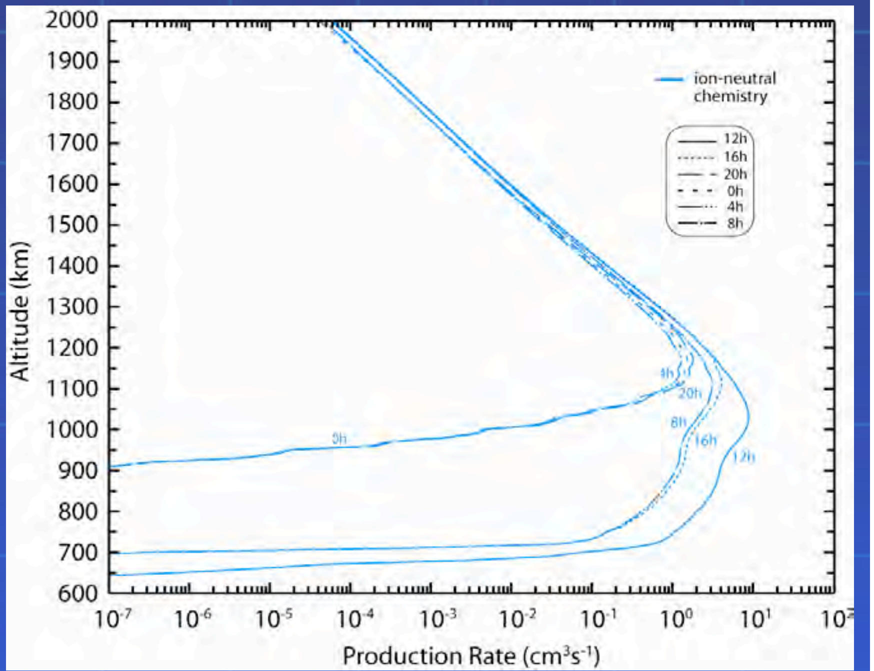
IV.4 The Composition:

the main ion-neutral scheme – production rates

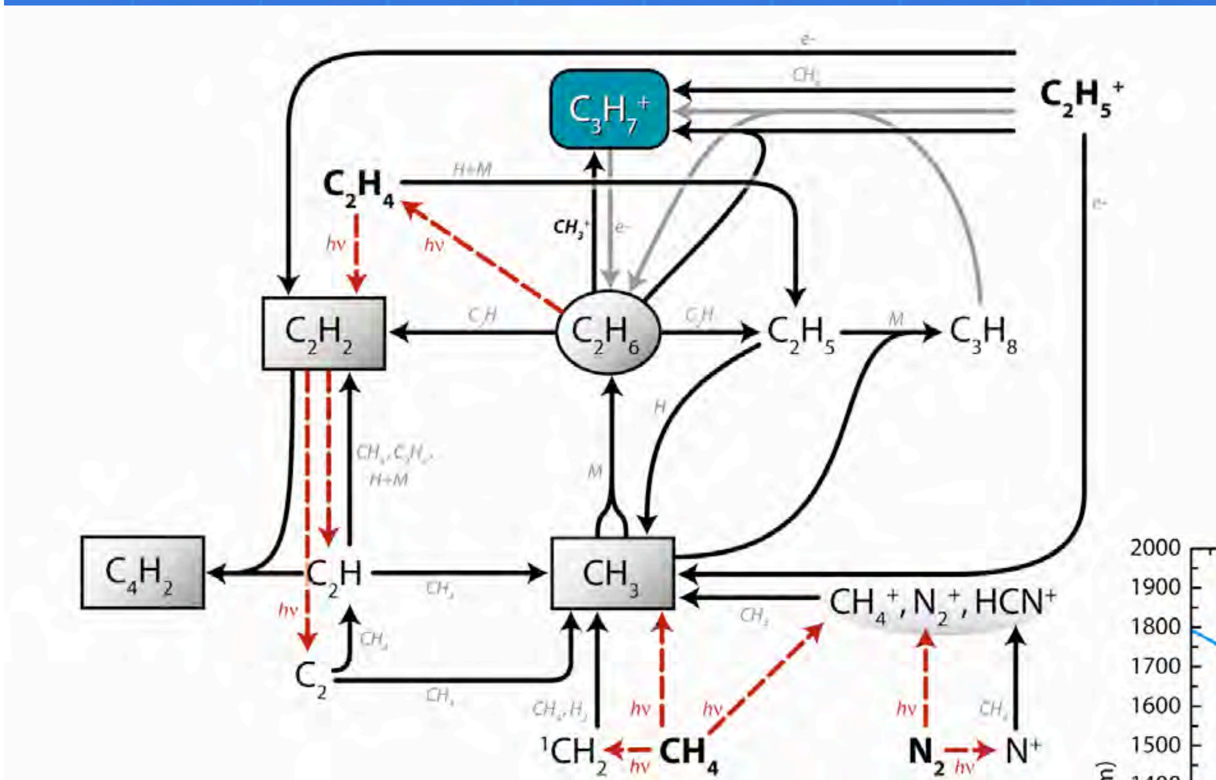


← Local time dependent production rates for C_2H_4

Local time dependent production rates → for H_2CN^+

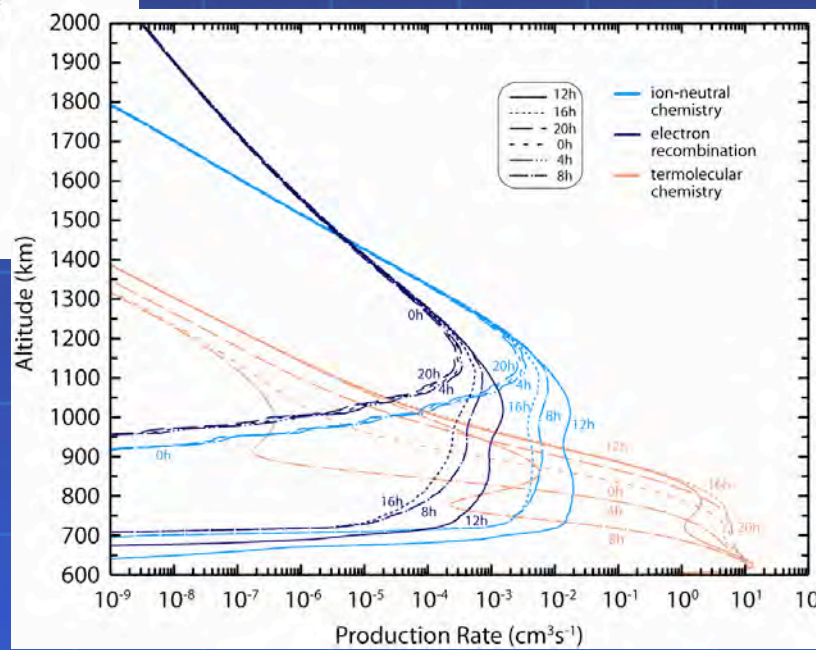


IV.5 The Composition:
subsequent production of key hydrocarbons



- **Production of hydrocarbons:**
  - C_2H_2
  - CH_3
  - C_2H_6
  - C_4H_2
  - C_3H_8 ,…

Local time dependent → production rates for C_2H_6

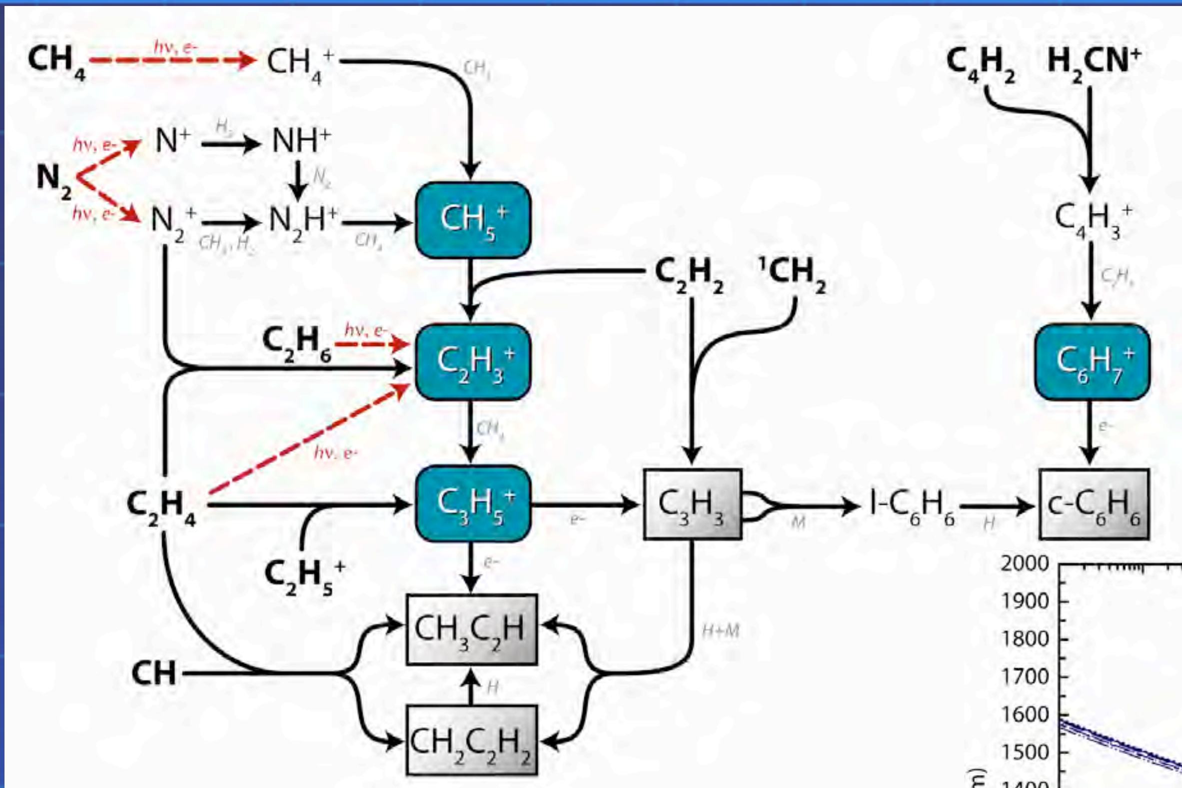


INMS: Neutrals (~ 1200 km)

Species	INMS (TA)
CH_4	3.3×10^{-2}
C_2H_2	2.8×10^{-4}
C_2H_6	1.2×10^{-4}
C_3H_4	4.0×10^{-6}
C_3H_8	2.3×10^{-6}

Waite et al. 2005

IV.6 The Composition:
production of heavy hydrocarbons and key ions

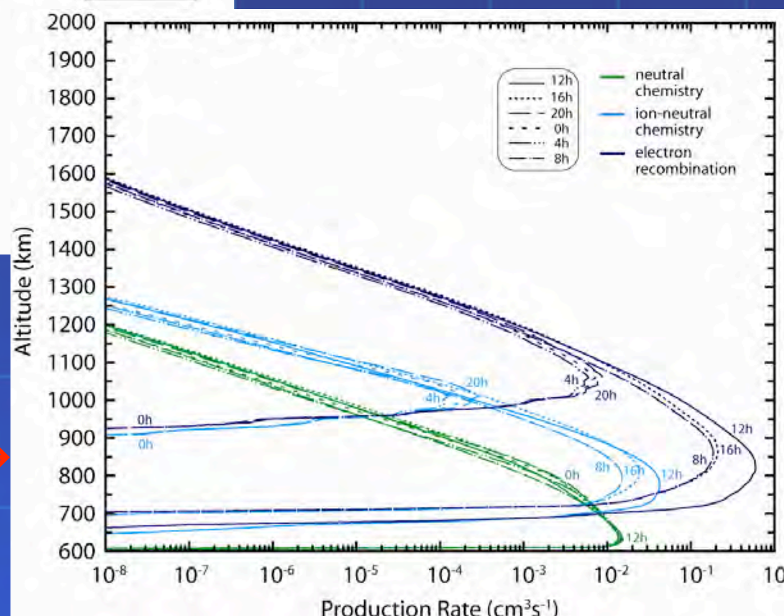


- **Production of**

Hydro- carbons:	Key ions:
– C_3H_3	– CH_5^+
– C_3H_4	– $C_2H_3^+$
– C_6H_6	– $C_3H_5^+$
	– $C_6H_7^+$

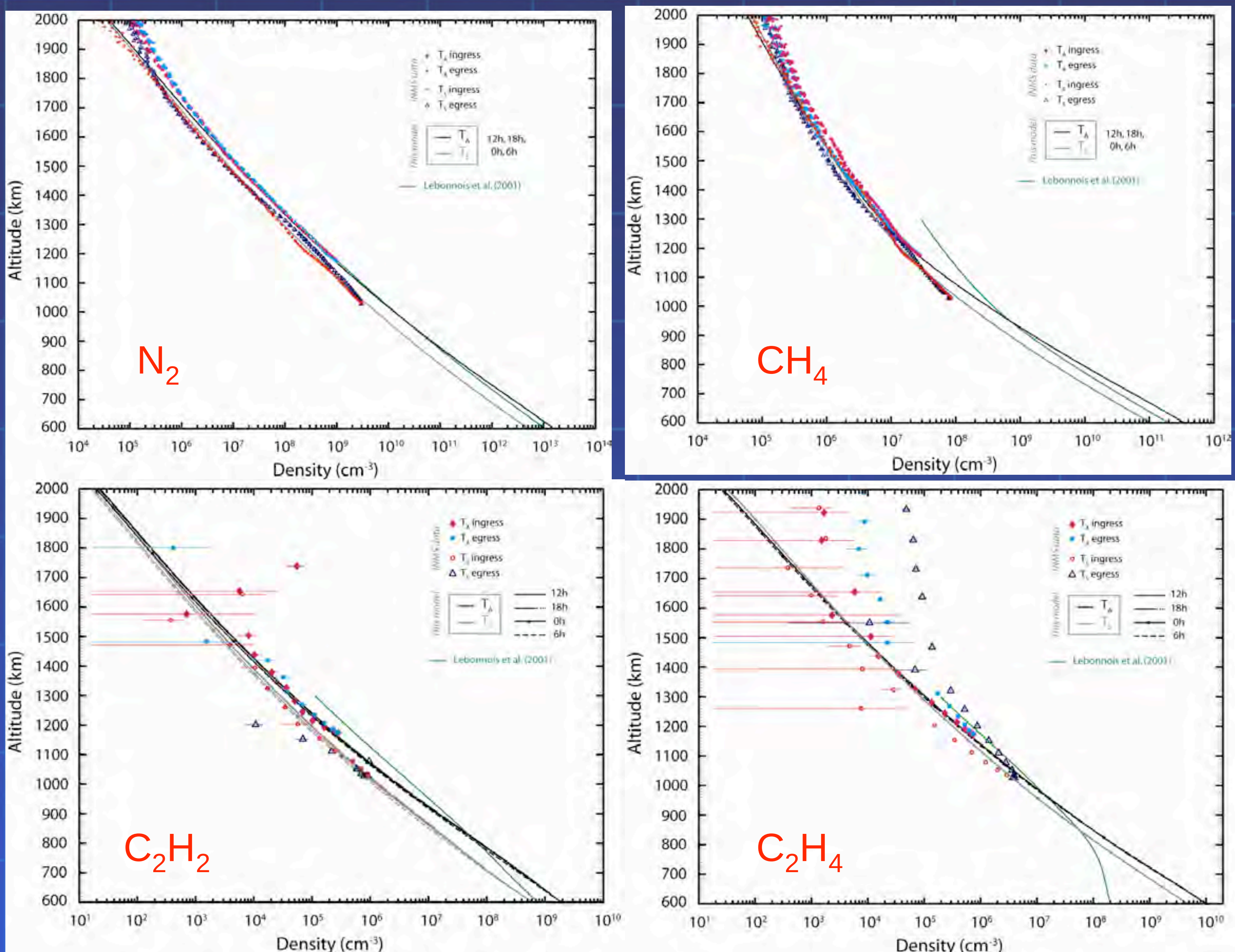
Local time dependent production rates →

for c-C_6H_6



IV.8 The Composition:

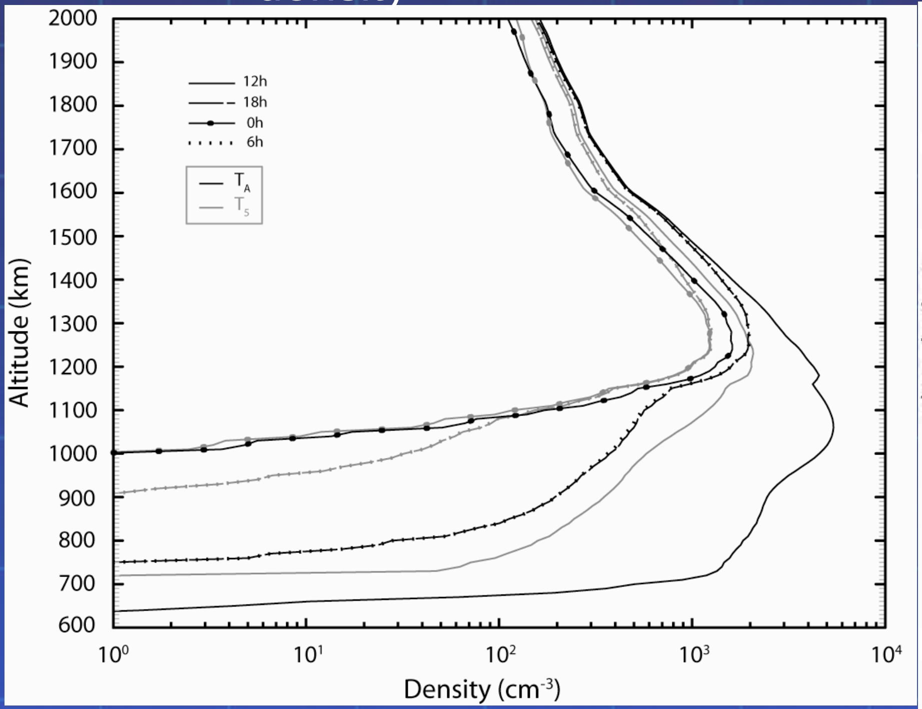
neutral results – local time dependent density profiles (1)



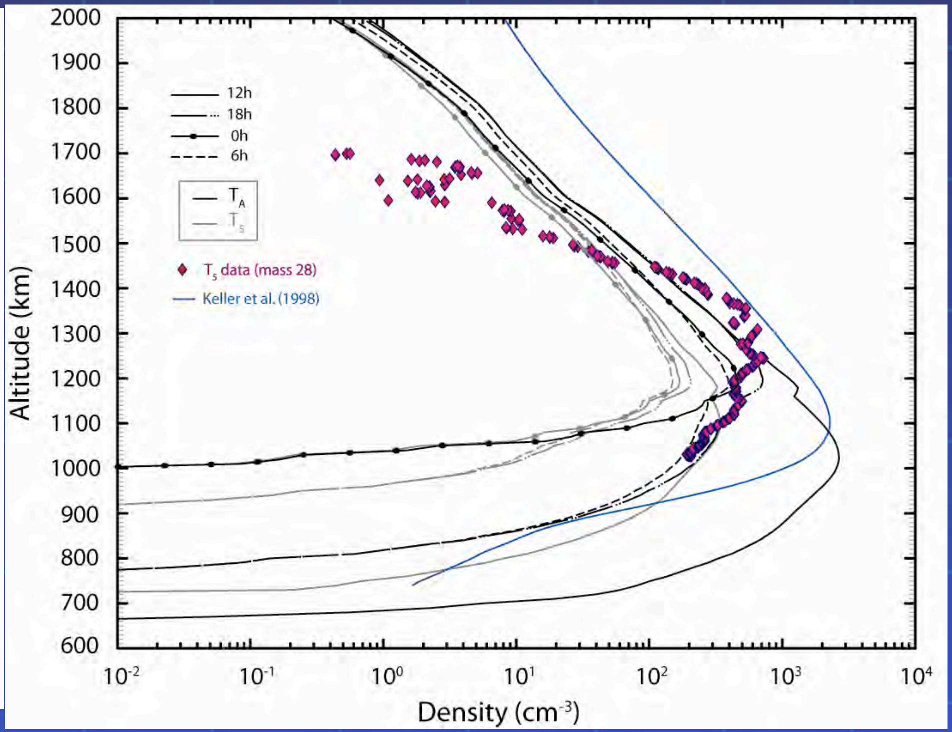
IV.10 The Composition:

ion results – local time dependent density profiles (1)

Electron density

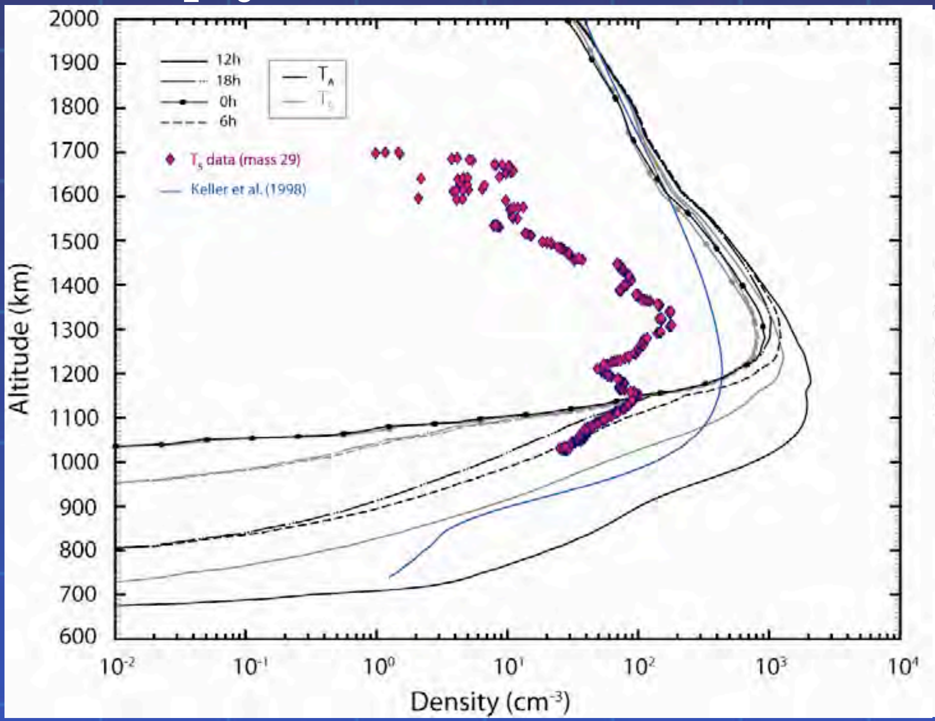


Density of H_2CN^+

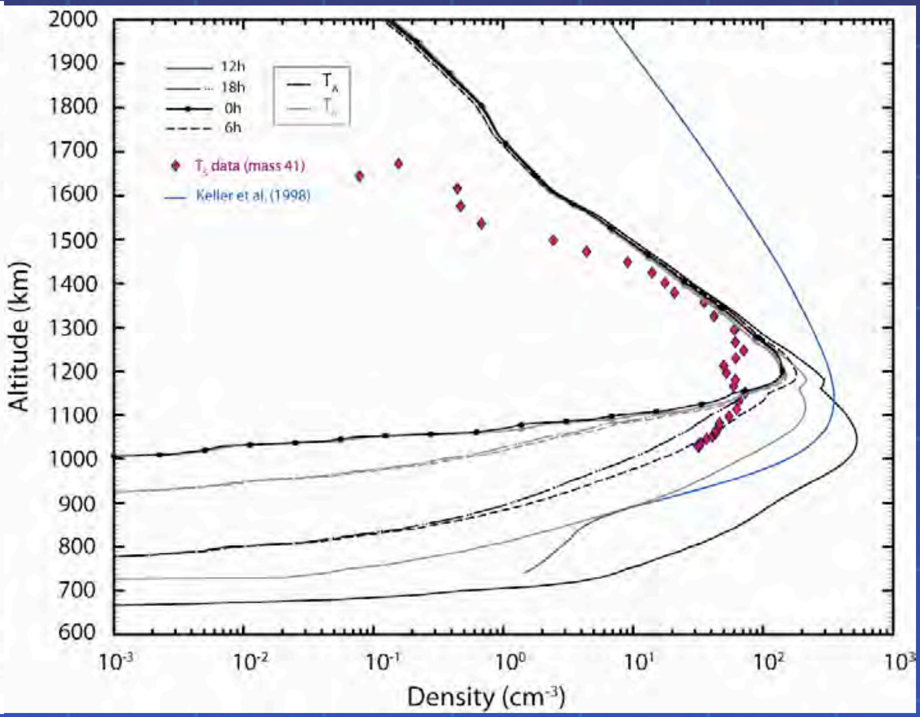


IV.11 The Composition:
ion results – local time dependent density profiles (2)

$C_2H_5^+$



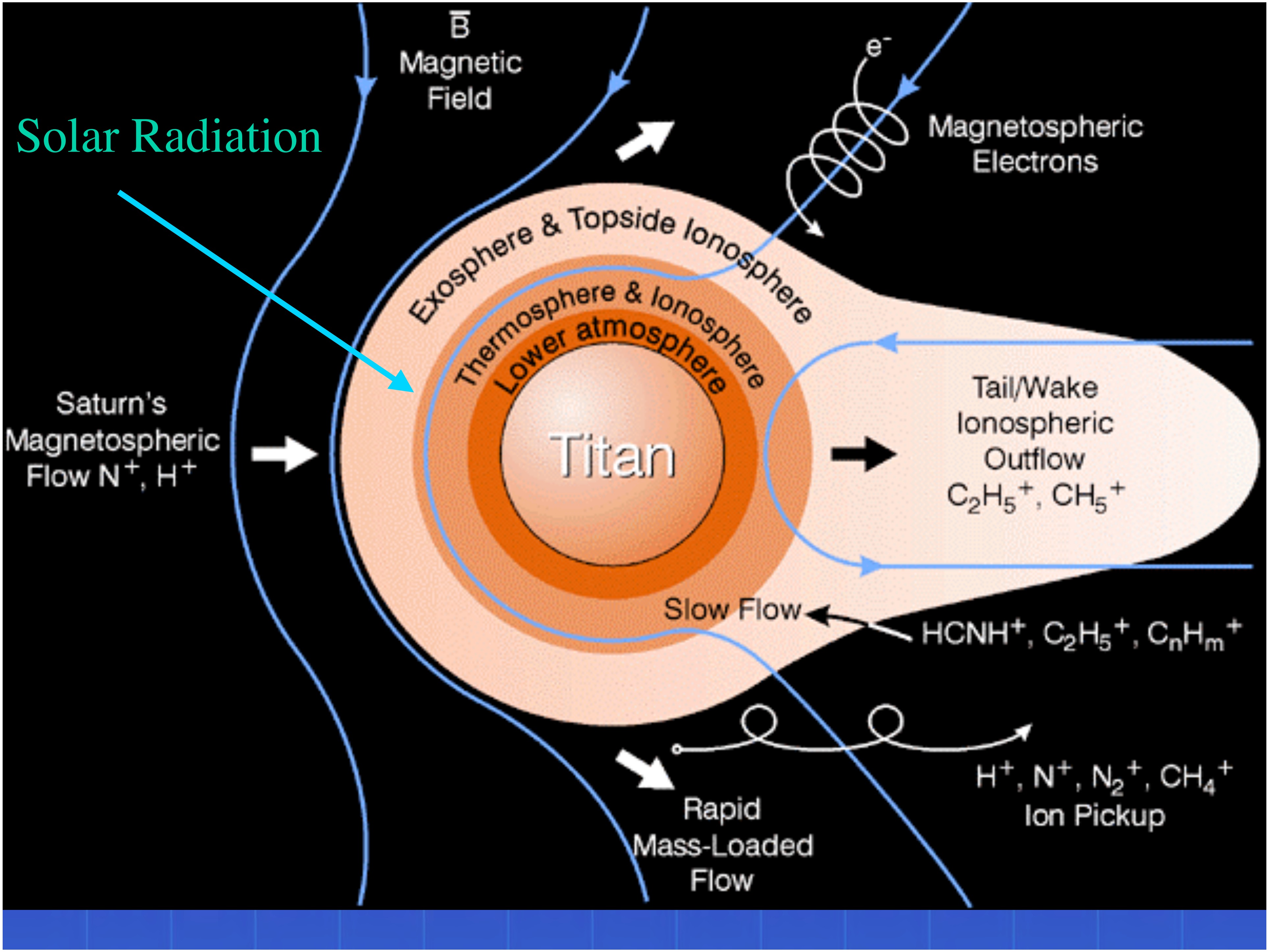
$C_3H_5^+$



Ion Neutral Mass Spectrometer

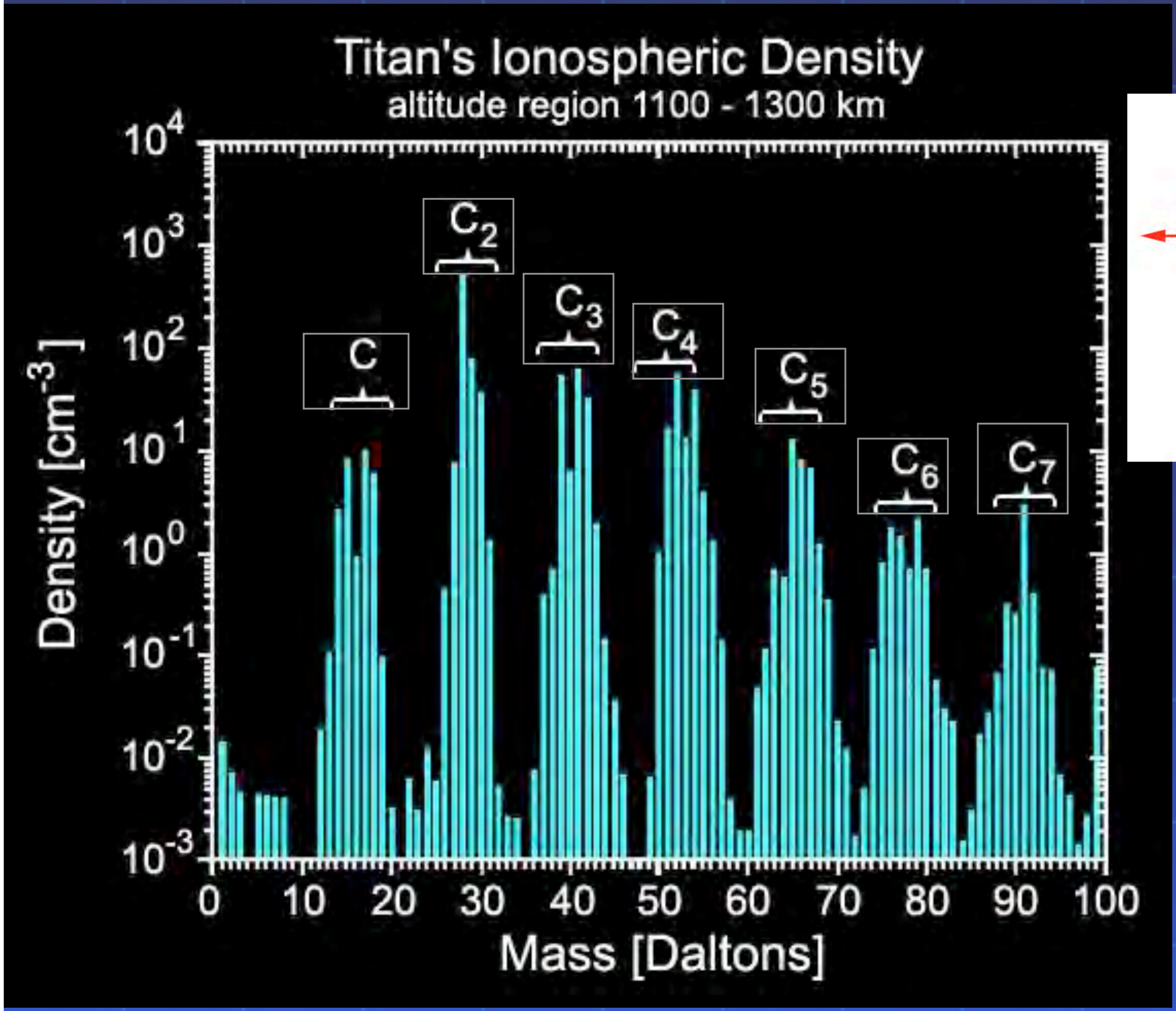
An Increased Role for the Magnetospheric Interaction

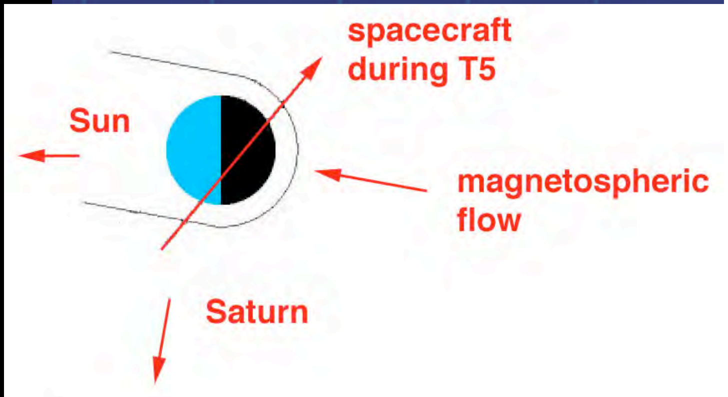
and Nitrile Ion Chemistry

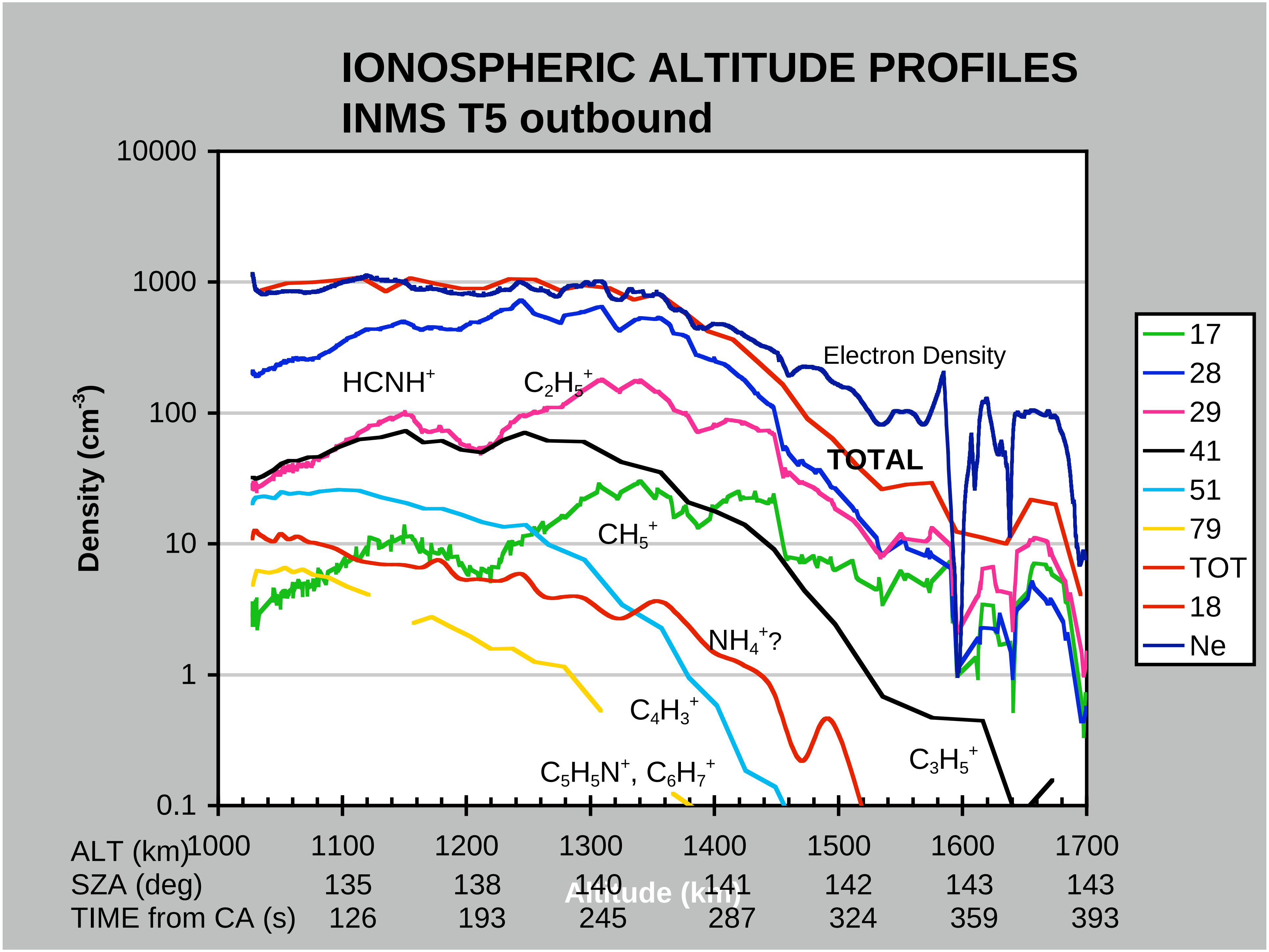


Solar Radiation
B̄
Magnetic
Field
e⁻
Magnetospheric
Electrons
Exosphere & Topside Ionosphere
Thermosphere & Ionosphere
Lower atmosphere
Titan
Saturn's
Magnetospheric
Flow N+, H+
Tail/Wake
Ionospheric
Outflow
C2H5+, CH5+
Slow Flow
HCNH+, C2H5+, CnHm+
H+, N+, N2+, CH4+
Ion Pickup
Rapid
Mass-Loaded
Flow

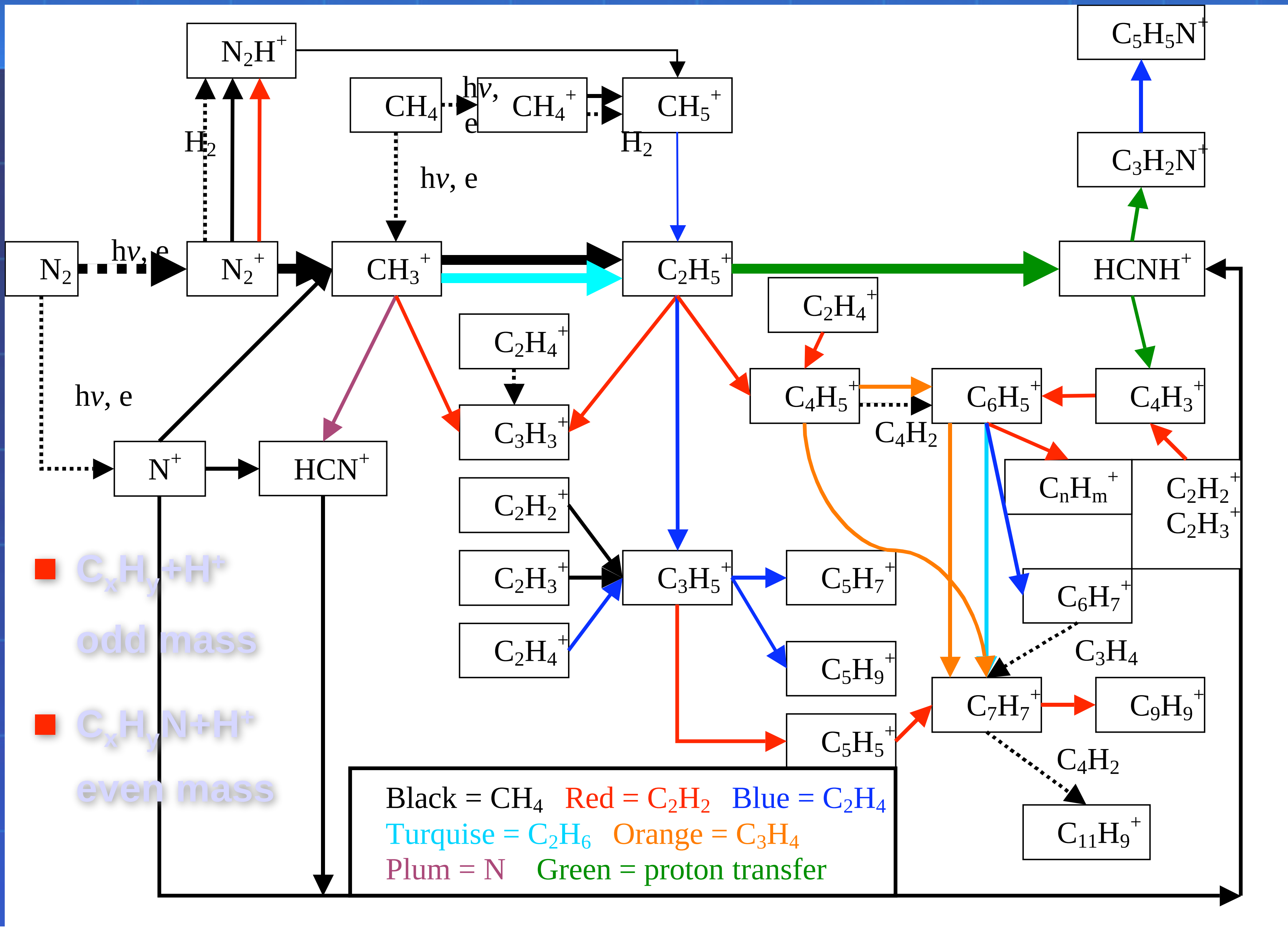
INMS: Ions (1100 - 1300 km)





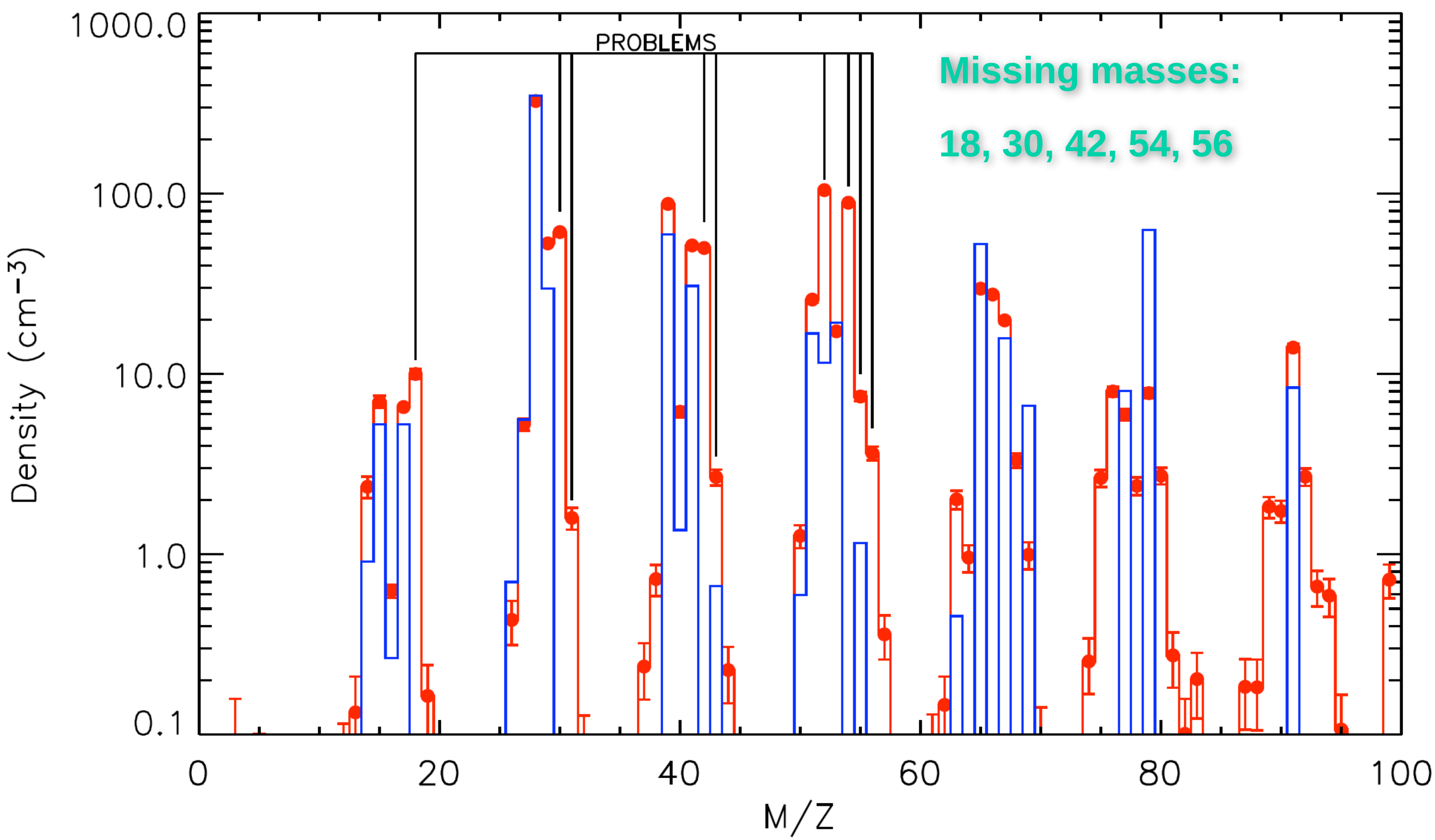

IONOSPHERIC ALTITUDE PROFILES
INMS T5 outbound
Density (cm-3)
10000
1000
100
10
1
0.1
HCNH+
C2H5+
Electron Density
TOTAL
CH5+
NH4+?
C4H3+
C5H5N+, C6H7+
C3H5+
17
28
29
41
51
79
TOT
18
Ne
ALT (km) 1000 1100 1200 1300 1400 1500 1600 1700
SZA (deg) 135 138 140 141 142 143 143
TIME from CA (s) 126 193 245 287 324 359 393
Altitude (km)

Keller et al. model flowchart

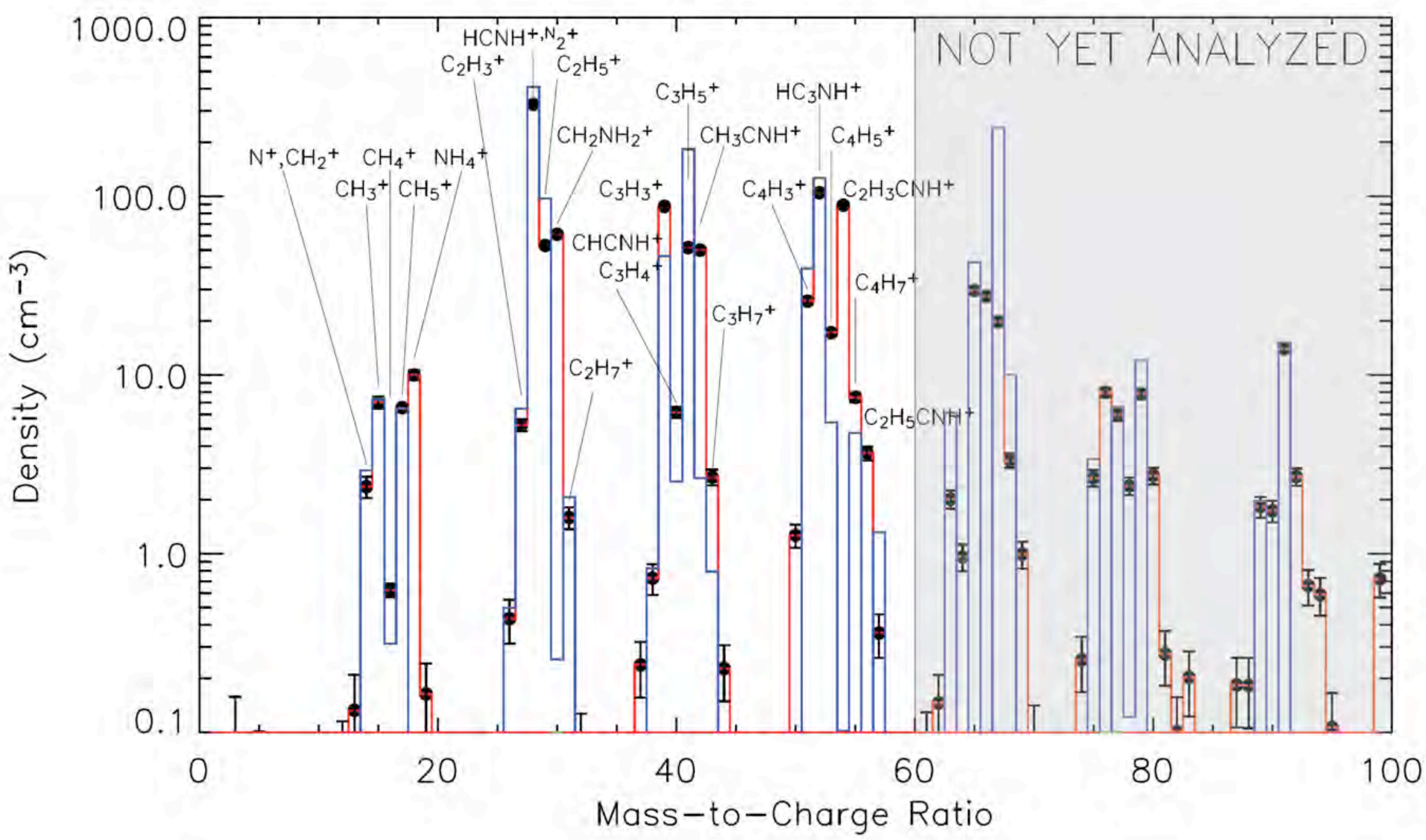


- C_xH_y+H$^+$ odd mass
- C_xH_yN+H$^+$ even mass

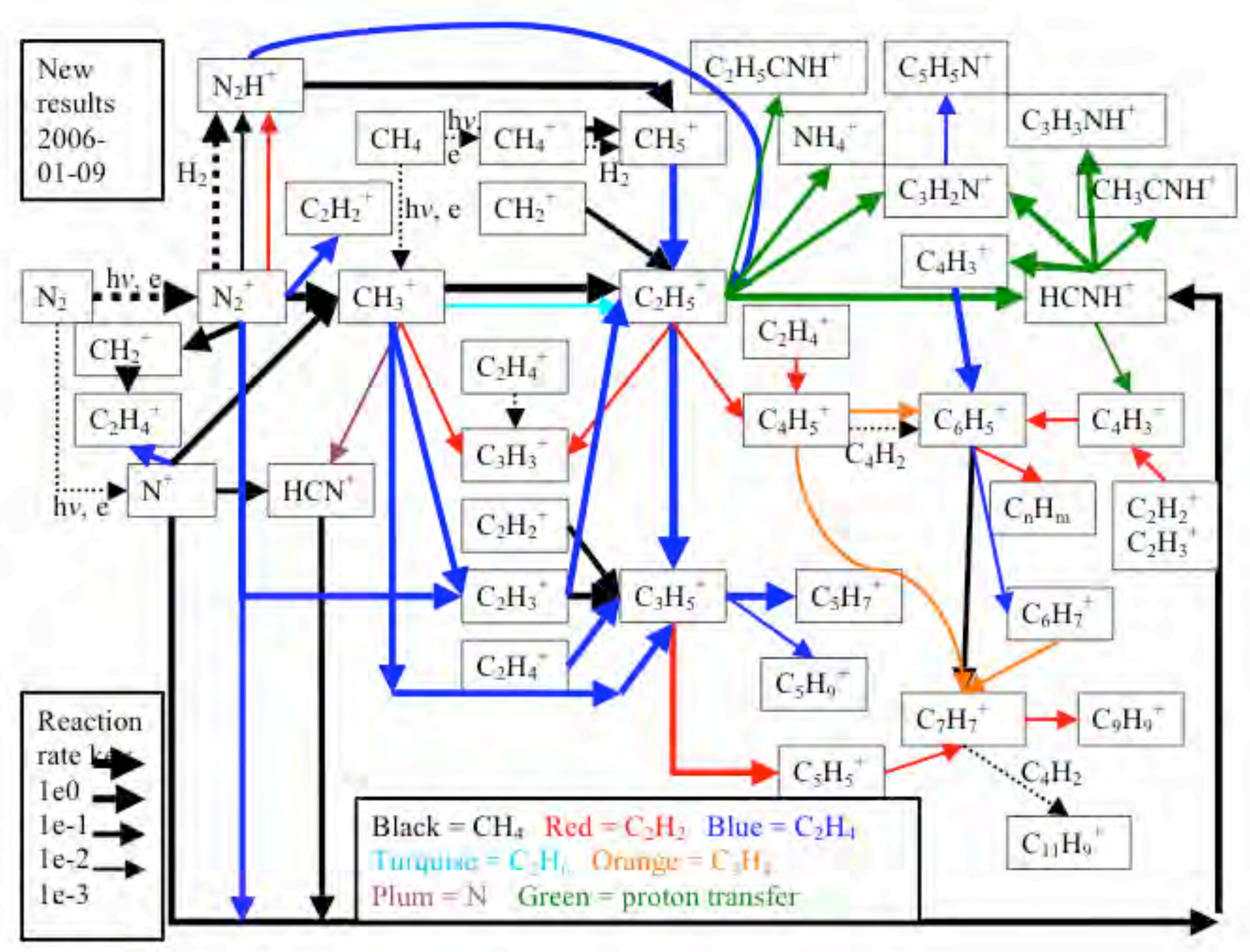
INMS / Keller et al. model



INMS / new Vuitton and Yelle model



New model flowchart



Ion Neutral Mass Spectrometer

Ultimate Fate of Complex Organics

Atmospheric Composition: Molar fractions estimated at 1174 km from the T_a data

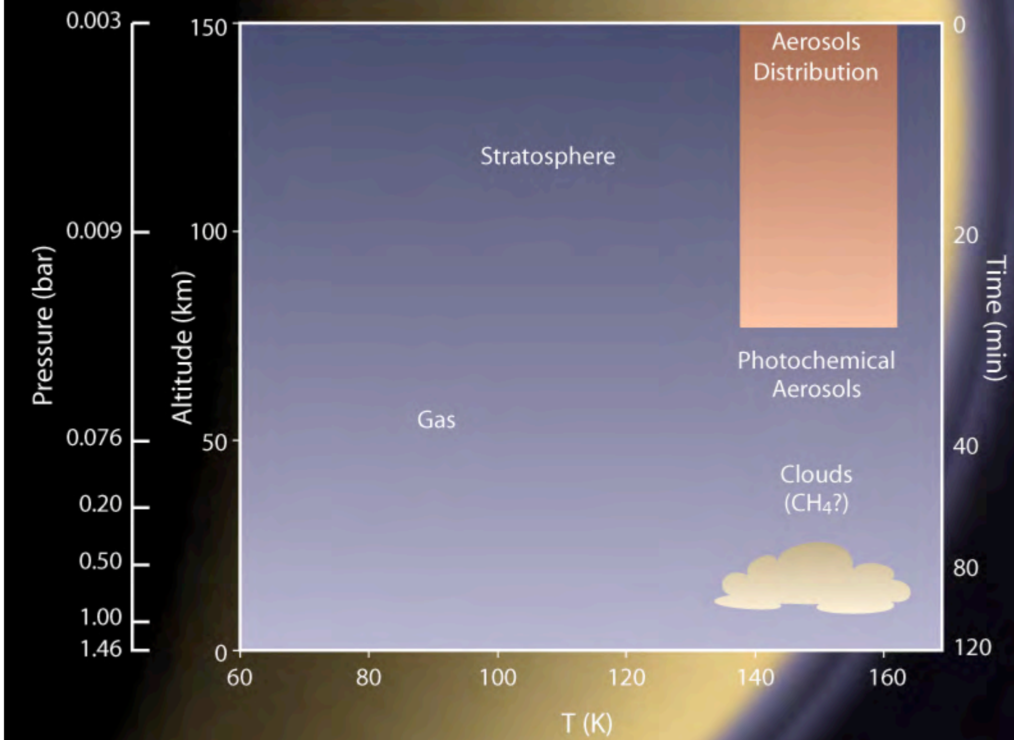
(Closed source)

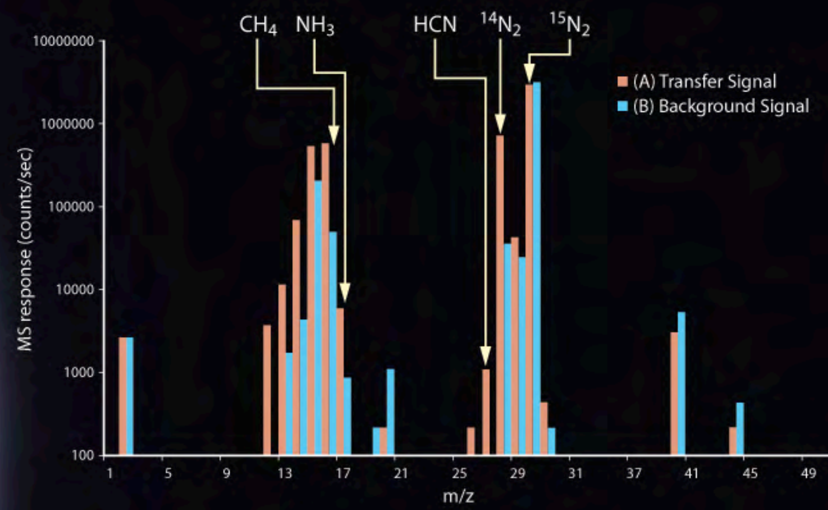
Minor species determined from the mass spectral deconvolution with one sigma error.

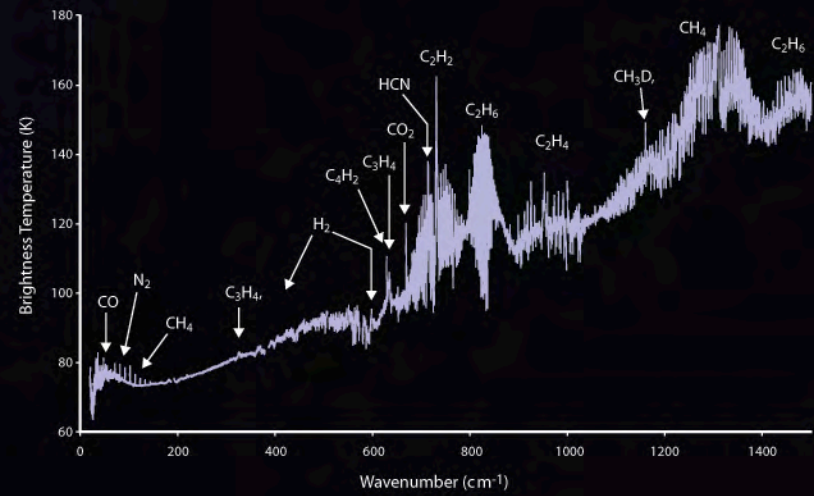
Species	INMS-Derived Values	Stratospheric Values (*1*)
CH_4	$2.19 \pm 0.002 \times 10^{-2}$	2.2×10^{-2}
H_2	$4.05 \pm 0.03 \times 10^{-3}$	1.1×10^{-3}
C_2H_2	$1.89 \pm 0.05 \times 10^{-4}$	2.2×10^{-6}
C_2H_4	$2.59 \pm 0.70 \times 10^{-4}$ – $5.26 \pm 0.08 \times 10^{-4}$	9.0×10^{-8}
C_2H_6	$1.21 \pm 0.06 \times 10^{-4}$	9.4×10^{-6}
C_3H_4	$3.86 \pm 0.22 \times 10^{-6}$	4.4×10^{-9}

C_2H_4 value depends on the value adopted for HCN.

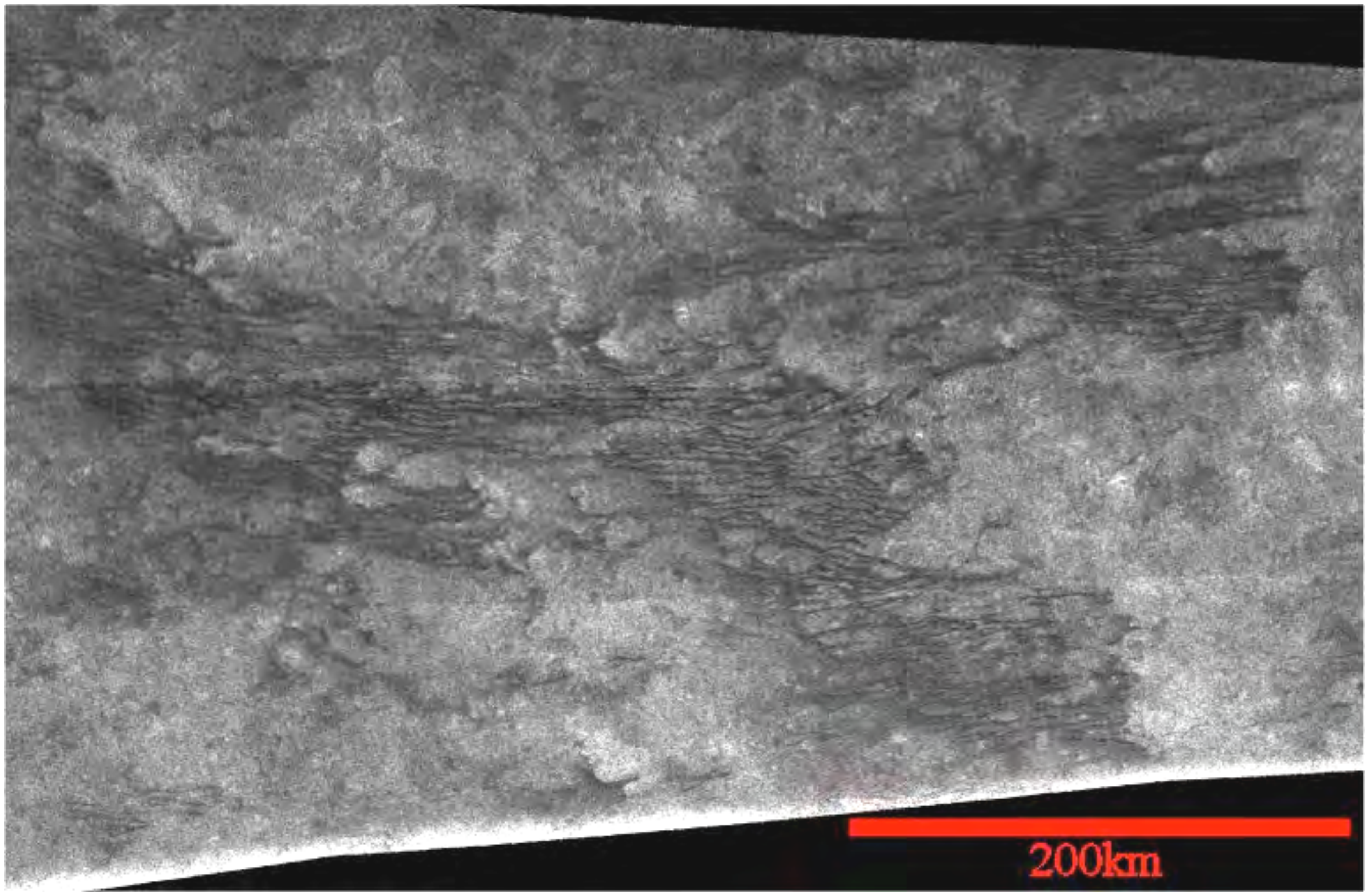
Stratospheric Composition







Cat Scratches



Acknowledgements

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- Radar Team
- Imaging Science Team
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- Composite Infrared Spectrometer Team
- Gas Chromatograph Mass Spectrometer Team
- SwRI Communications Department

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