Cassini-INMS: Observations of Titan and Enceladus

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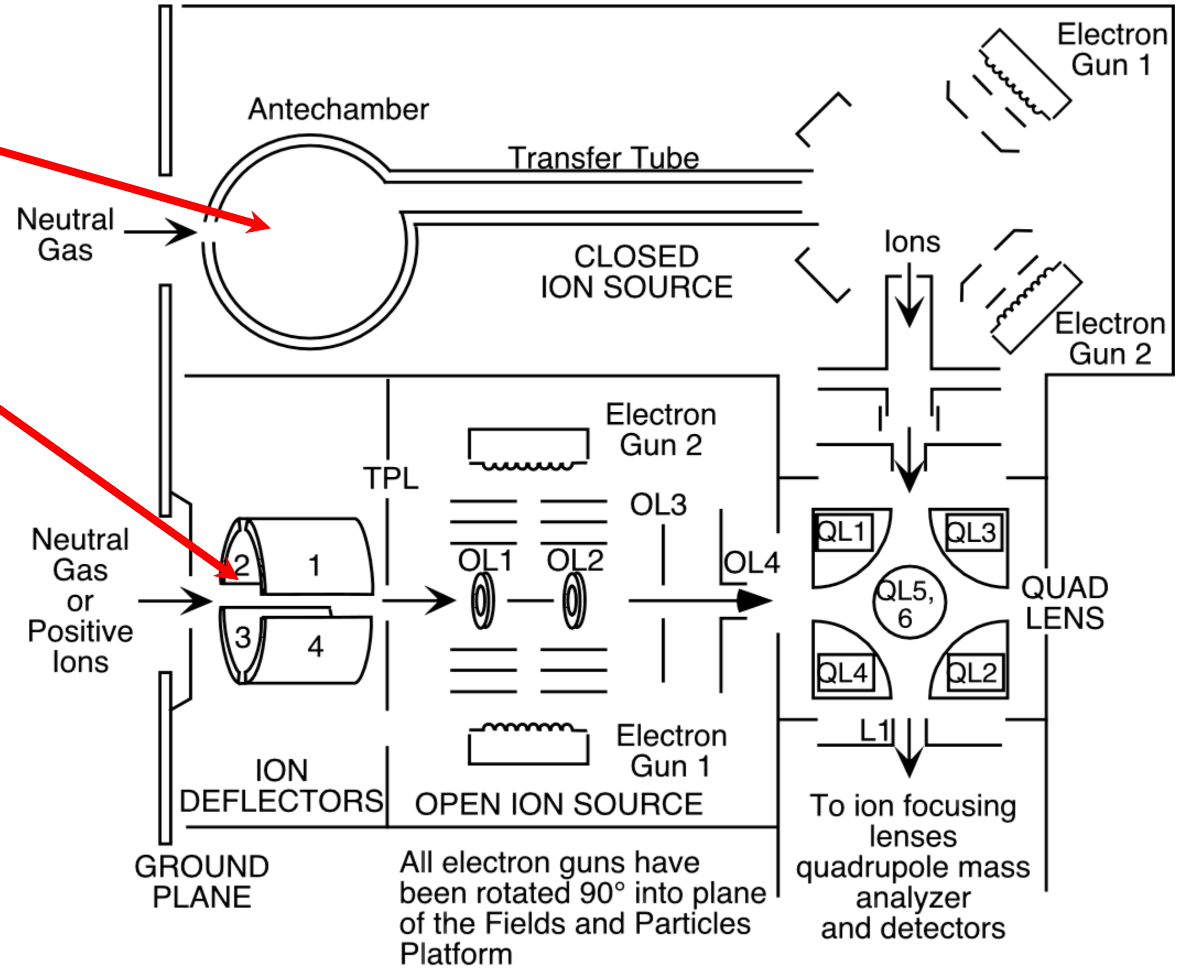
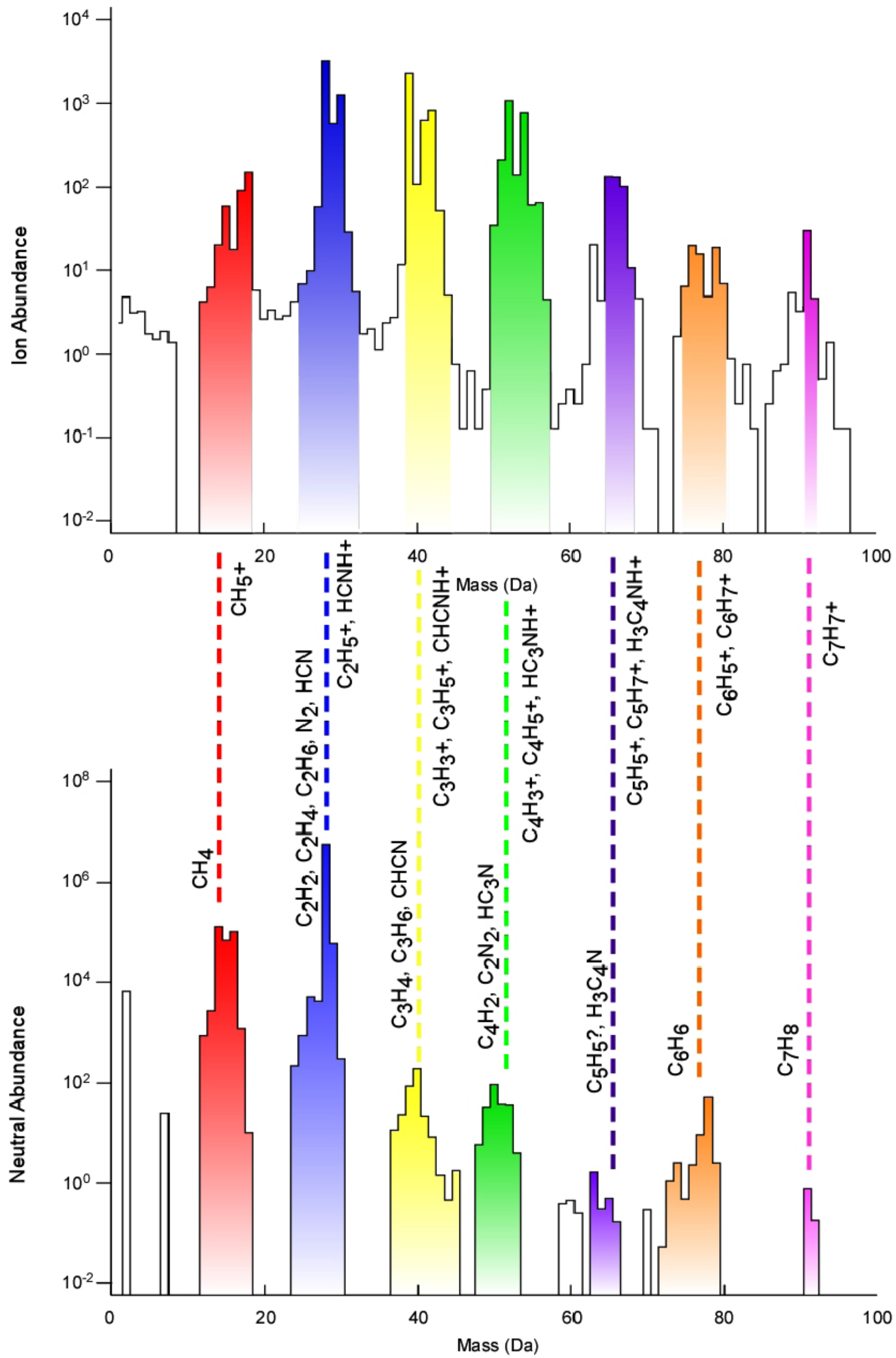
Ion Neutral Mass Spectrometer Instrument Configuration

During the Saturn moon flybys:

-Neutral densities from closed source

- Ion densities from open source





Mass Spectrum Data recorded by INMS

Ion spectrum
Ambient positively charged molecules enter the open source aperture and proceed through to the quadrupole mass analzyer.

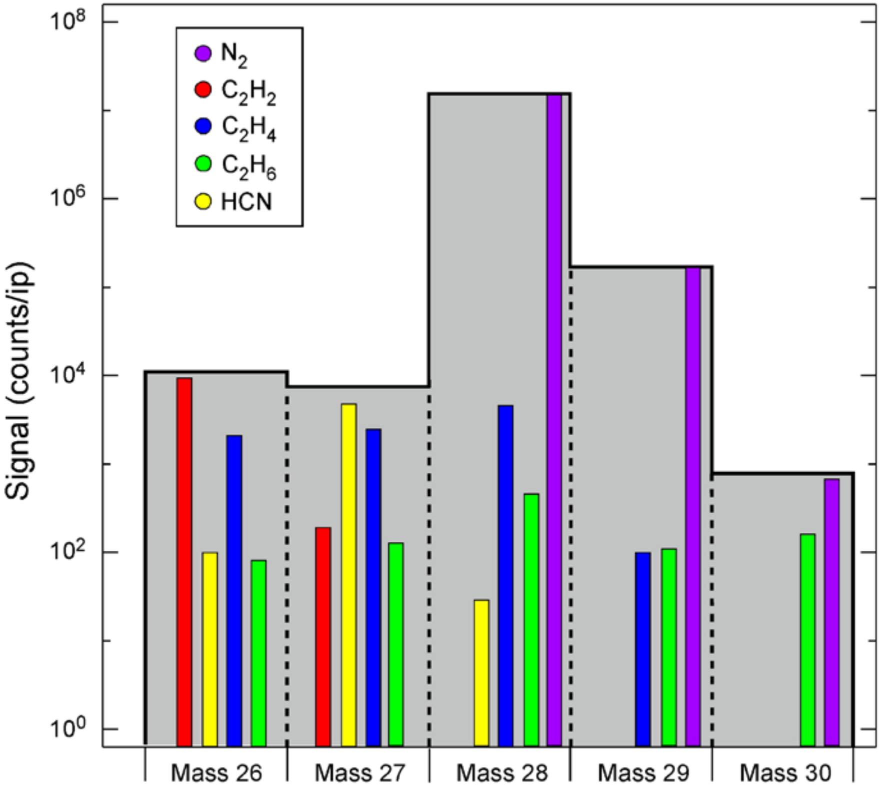
Neutral spectrum
Ambient molecules enter the closed source, thermally equilibrate in the antechamber and proceed to the ionization source. Neutrals are converted to positive ions through electron impact and are filtered by the mass analyzer.

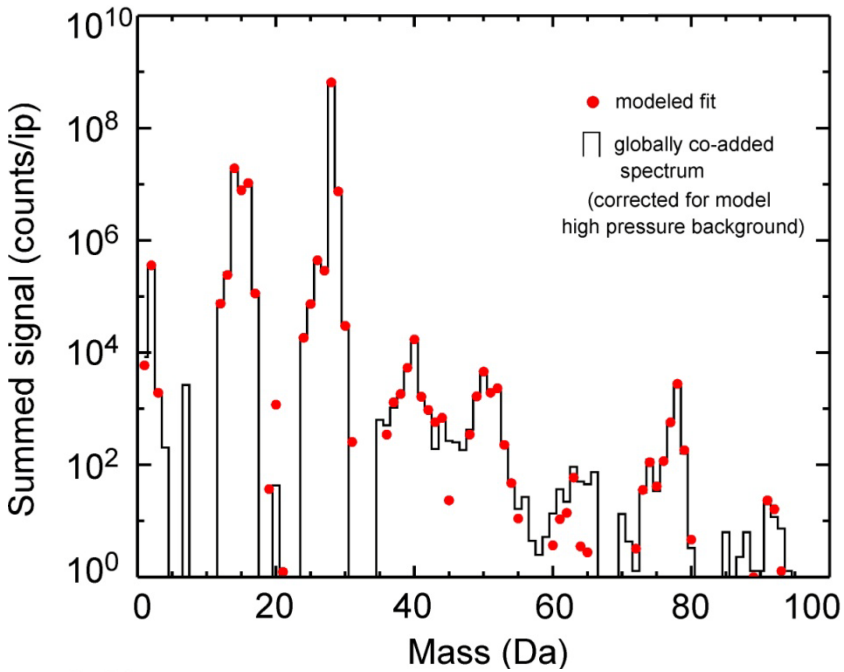
INMS Data Analysis

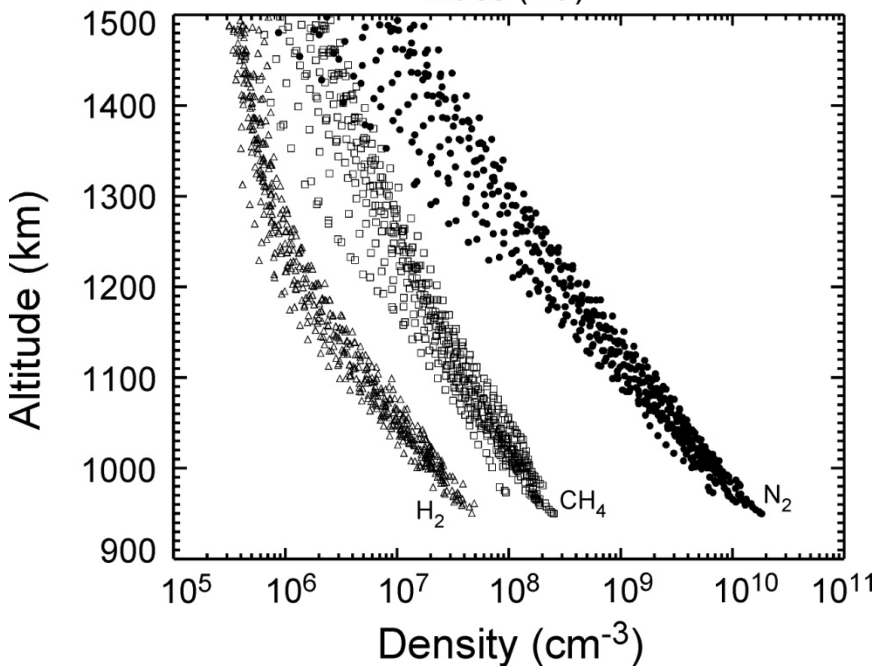
- Analysis returns depend on data viability, calibration, complexity of species mix, and a priori knowledge of sample.
- Electron-impact ionization of neutral molecules result not only in positively charged versions of the parent molecule, but ionized dissociative products as well.
- Overlapping spectral signatures make identification of individual species difficult.

Example of analysis difficulty:

C_2 organic signatures occupy most of the same mass bins. At Titan the C_2 organics have similar abundances and are further masked by a dominant N_2 signal, making it difficult to single out the individual species.



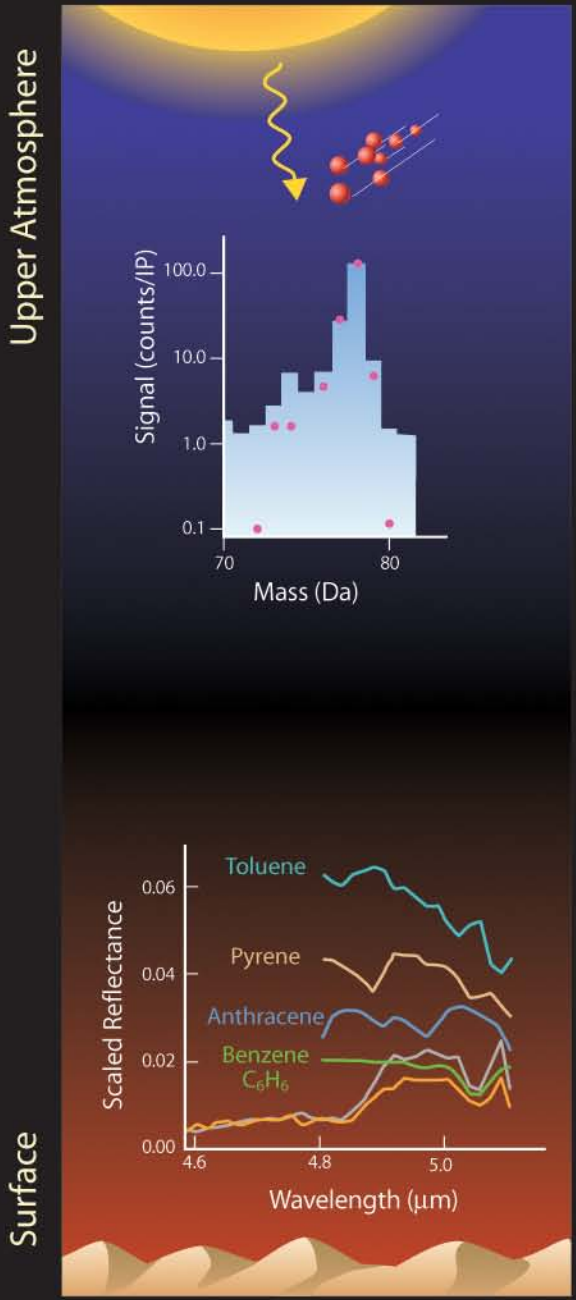


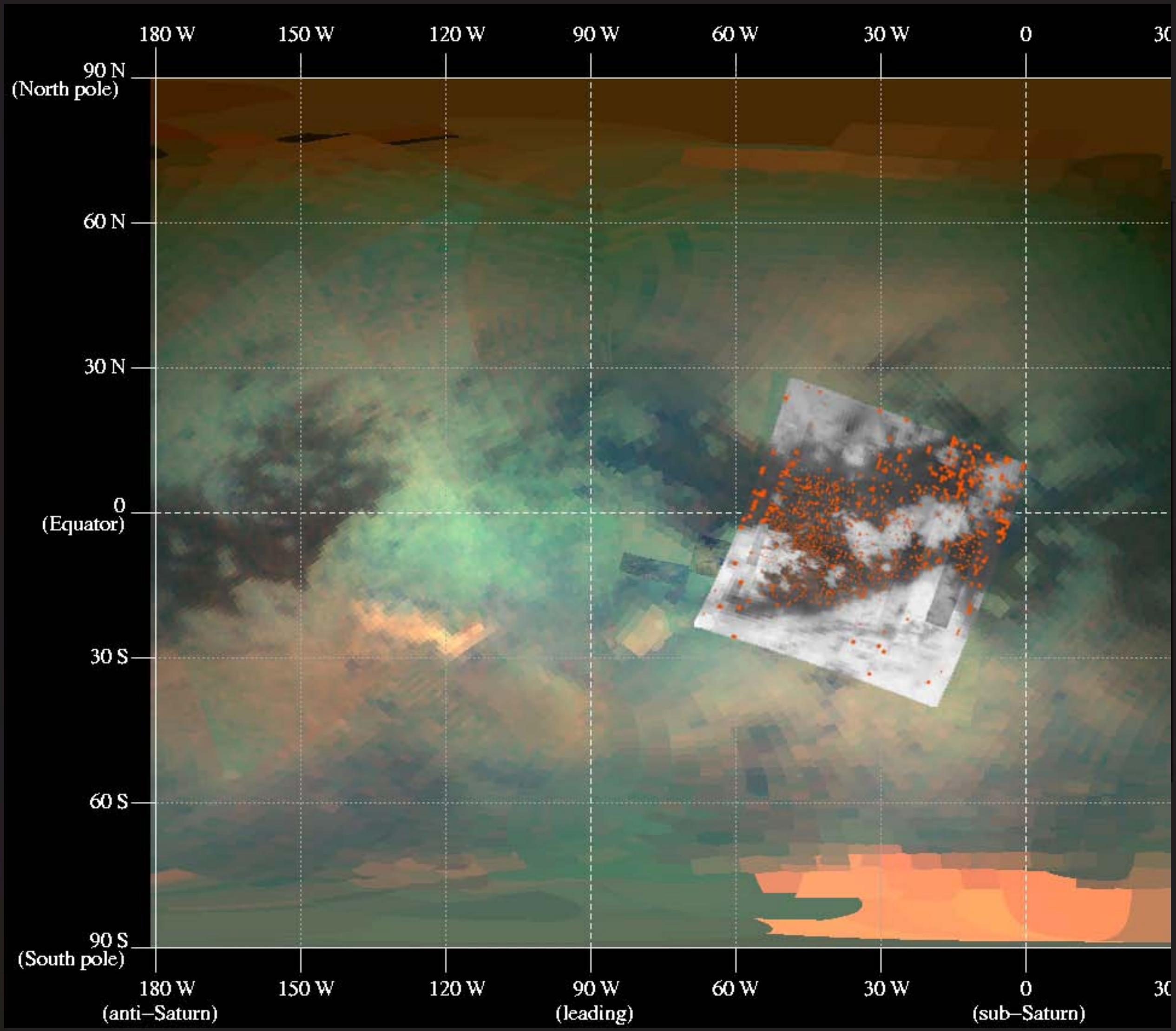


Magee et al. (2009)

Species	Mixing Ratio at 1050km
N_2	(96.3 ± 0.44) %
$^{14}N^{15}N$	(1.08 ± 0.06) %
CH_4	(2.17 ± 0.44) %
$^{13}CH_4$	(2.52 ± 0.46) x 10^{-4}
H_2	(3.38 ± 0.23) x 10^{-3}
C_2H_2	(3.42 ± 0.14) x 10^{-4}
C_2H_4	(3.91 ± 0.16) x 10^{-4}
C_2H_6	(4.57 ± 0.74) x 10^{-5}
HCN	(2.44 ± 0.10) x 10^{-4}
^{40}Ar	(1.26 ± 0.05) x 10^{-5}
CH_3C_2H	(9.20 ± 0.46) x 10^{-6}
C_3H_6	(2.33 ± 0.18) x 10^{-6}
C_3H_8	(2.87 ± 0.26) x 10^{-6}
C_4H_2	(5.55 ± 0.25) x 10^{-6}
C_2N_2	(2.14 ± 0.12) x 10^{-6}
HC_3N	(1.48 ± 0.09) x 10^{-6}
C_2H_3CN	(3.46 ± 0.51) x 10^{-7}
C_2H_5CN	(1.54 ± 0.48) x 10^{-7}
C_6H_6	(2.48 ± 0.11) x 10^{-6}
C_7H_8	(2.51 ± 0.95) x 10^{-8}
Density (cm^{-3})	(3.18 ± 0.71) x 10^{9}

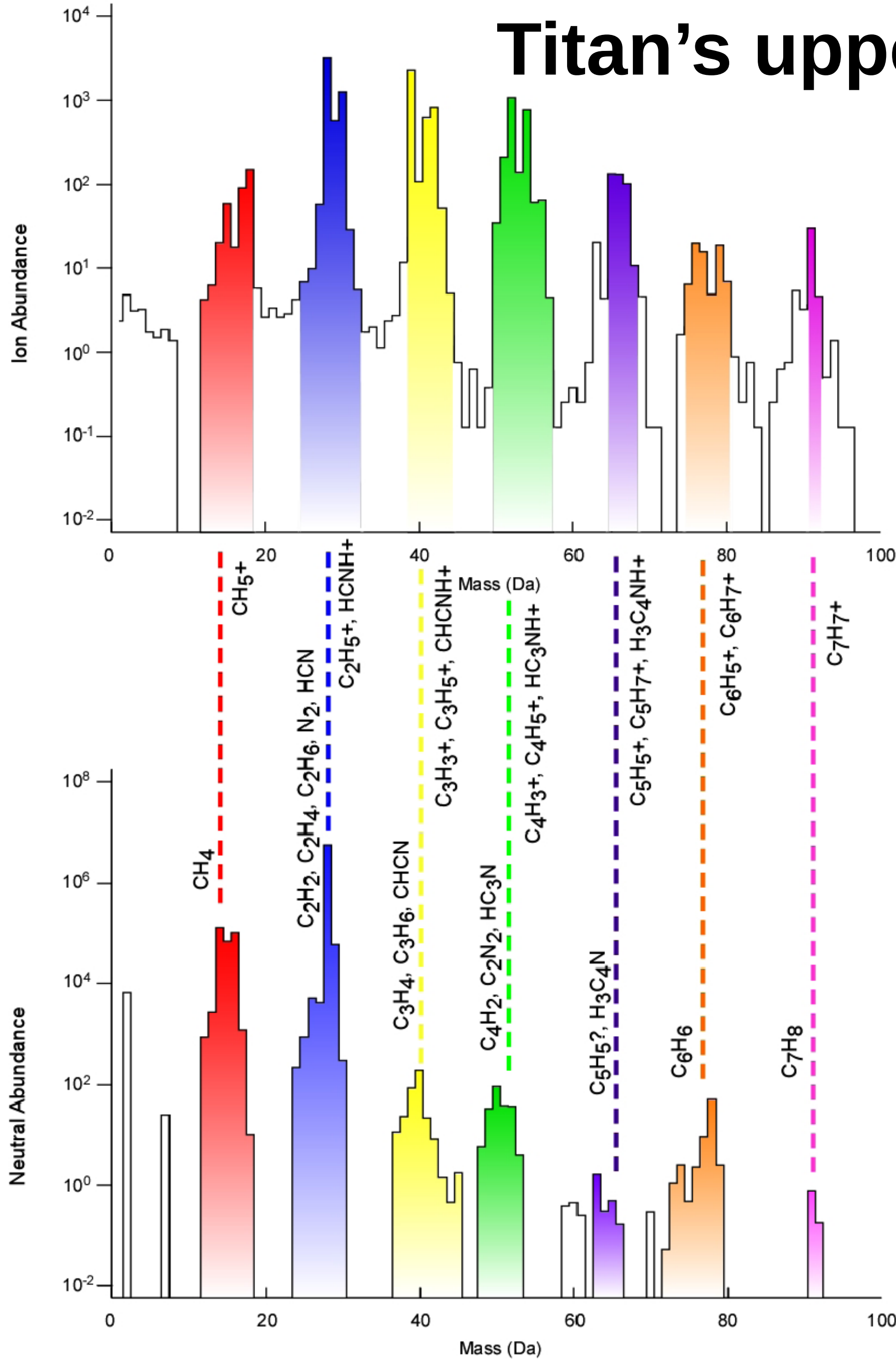
VIMS

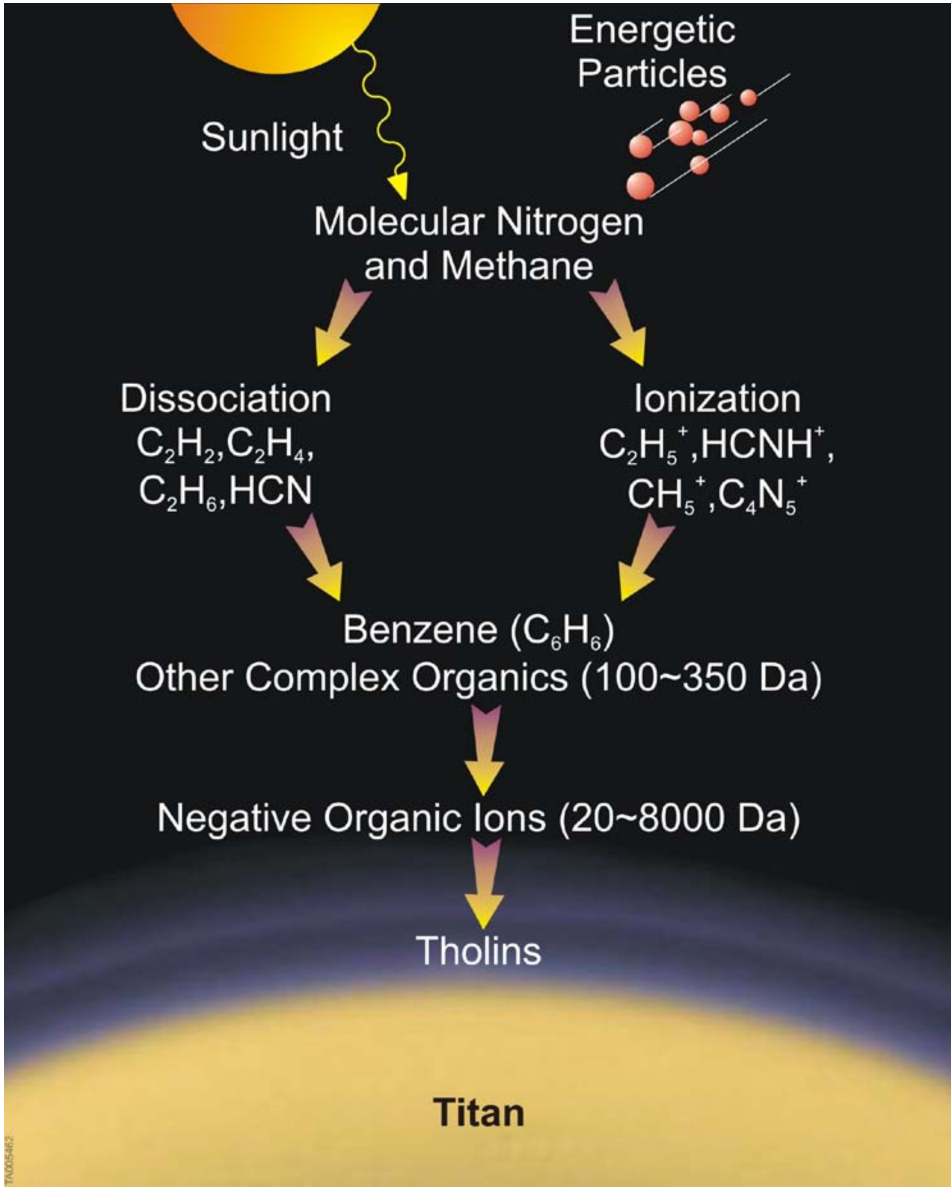




Benzene is detected by VIMS on the surface of Titan, primarily around the low latitude dune regions.

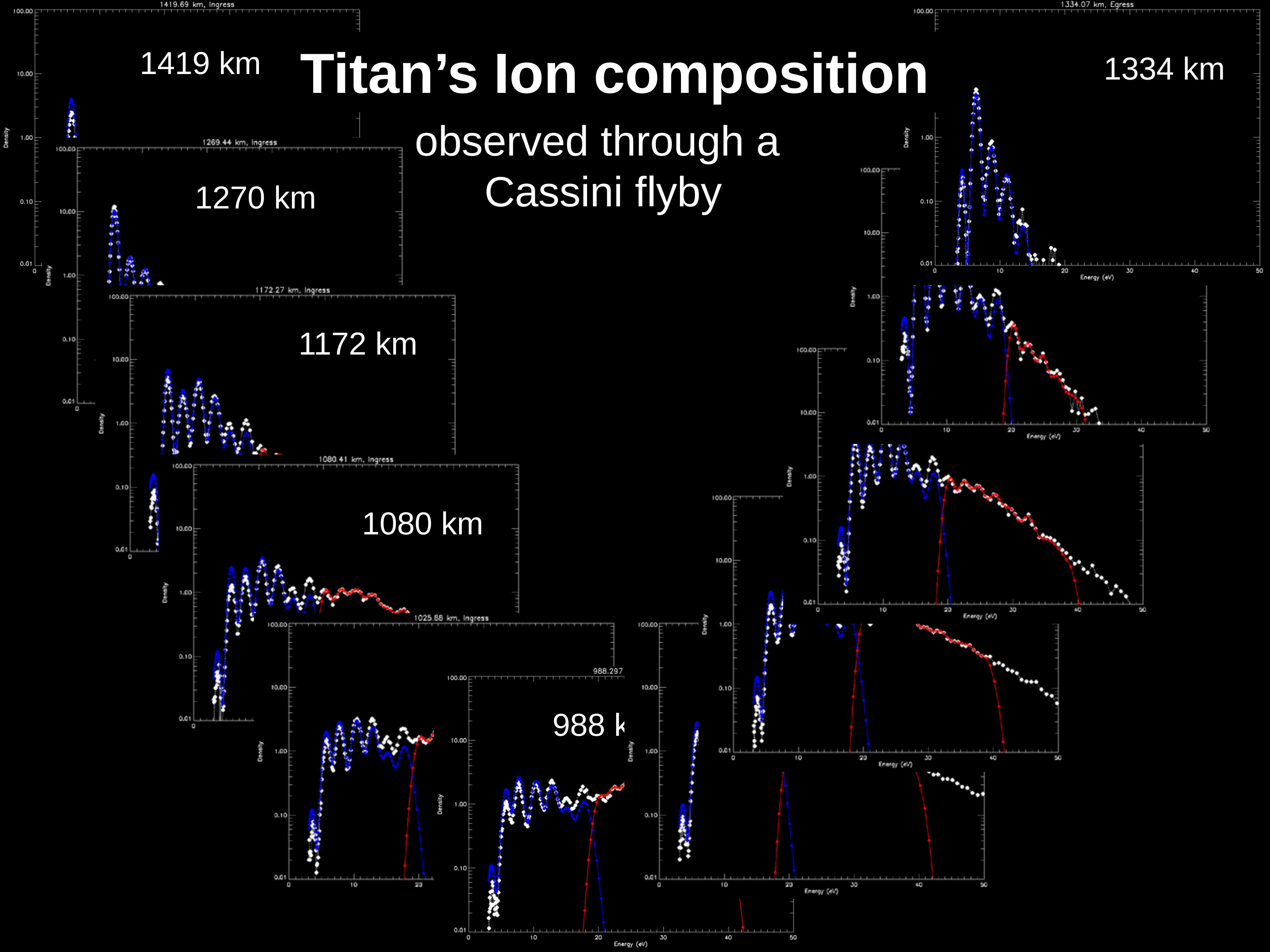
Titan's upper atmospheric chemistry



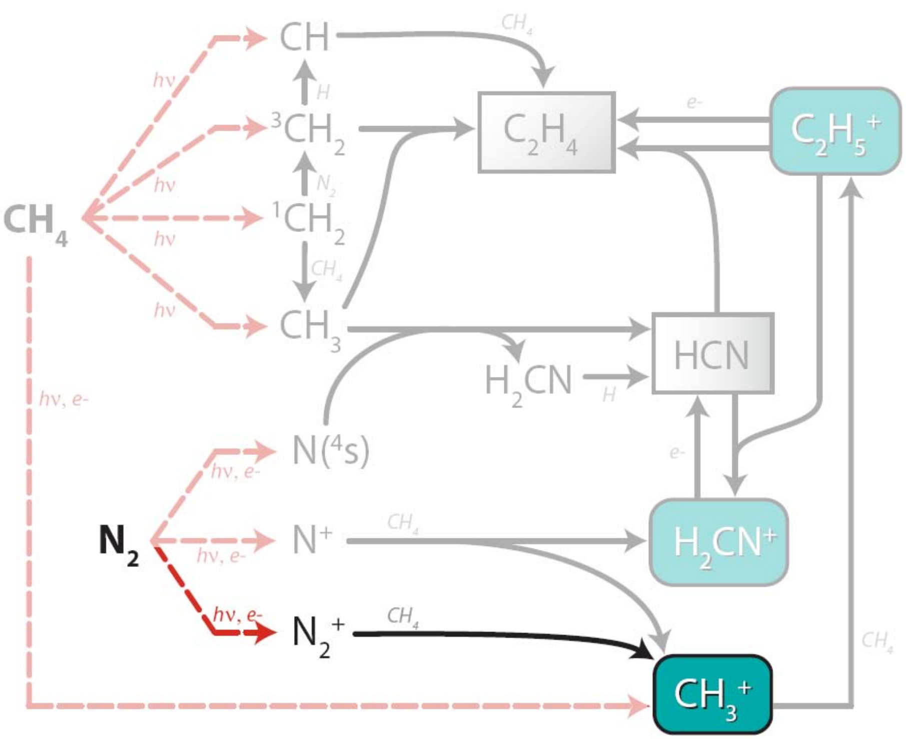


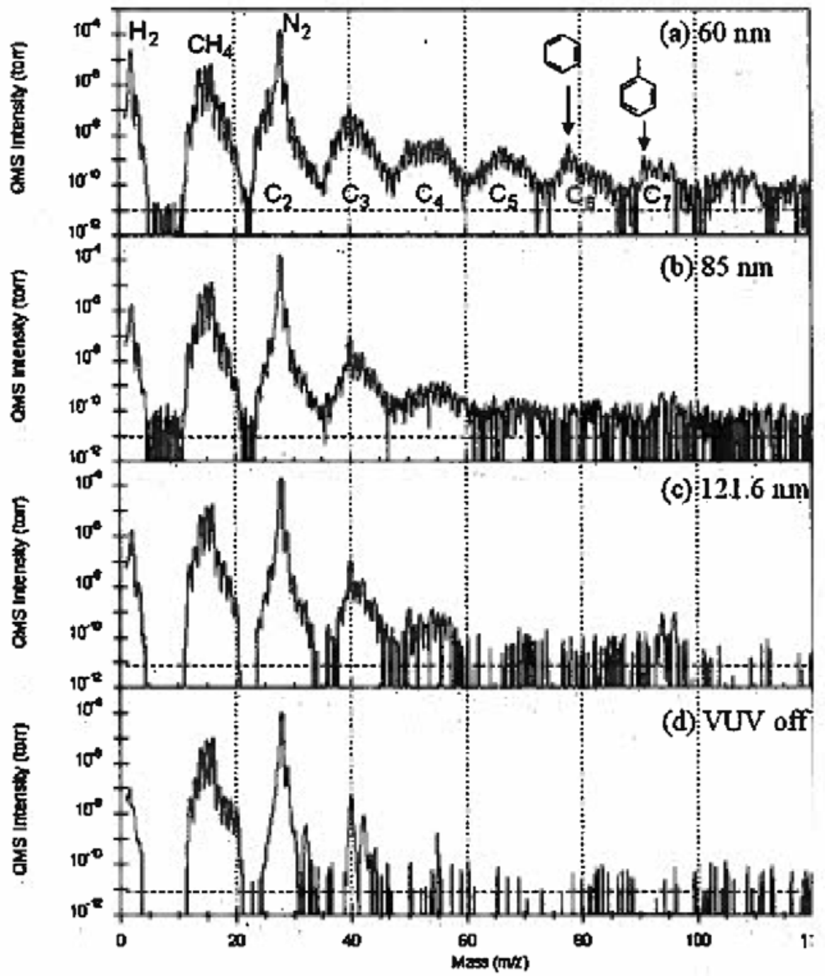
Titan's Ion composition

observed through a Cassini flyby



Titan's Nitrogen Photochemistry

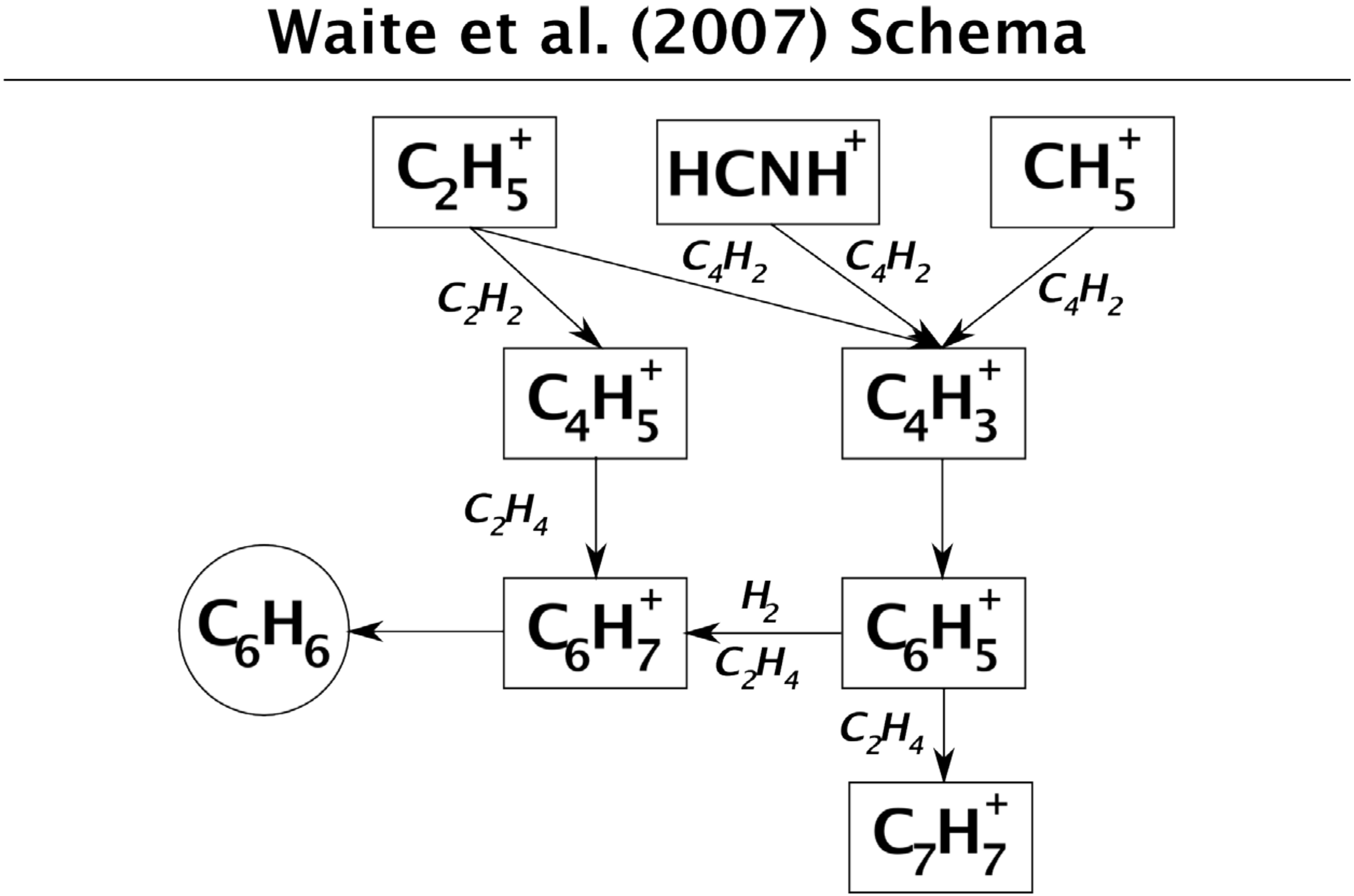




De La Haye et al. (2008)

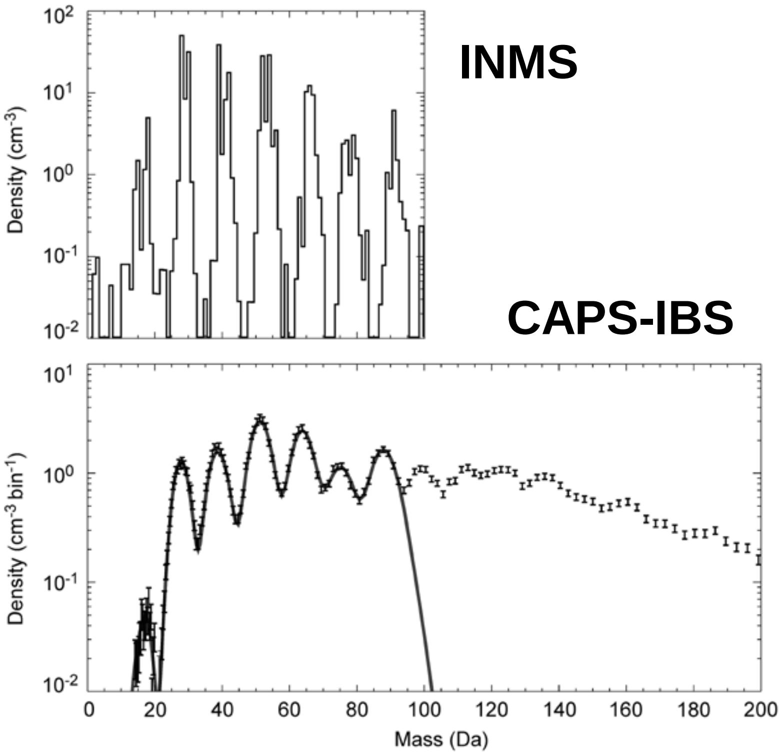
Imanaka and Smith (2007)

Benzene Formation



Positive Ions

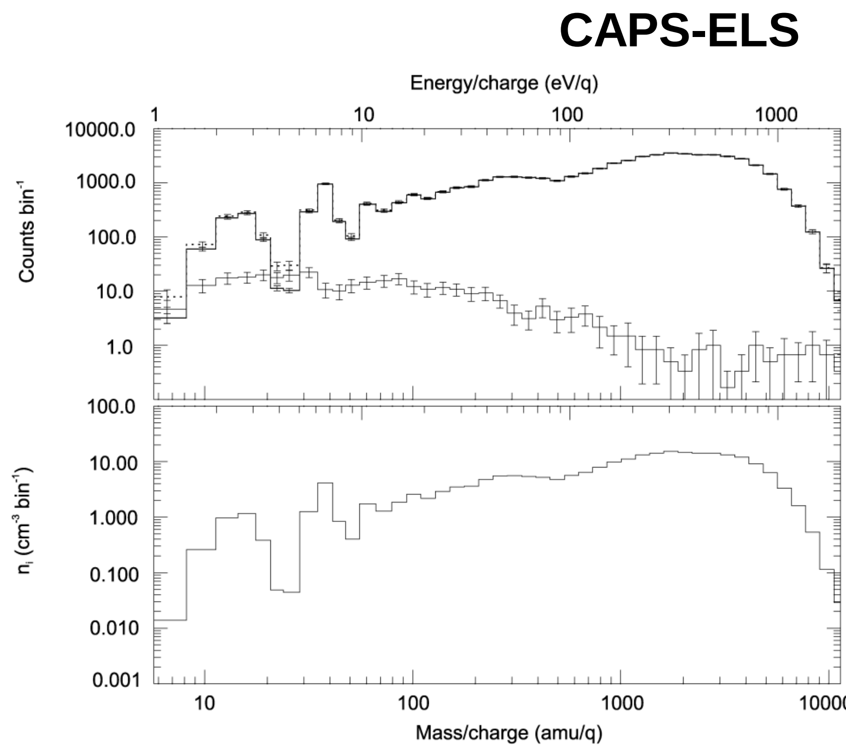
Masses up to ~350 Da.



Waite et al. (2007), Crary et al. (2009)

Negative Ions

Masses up to ~10,000 Da.



Coates et al. (2007)

GROUP	ALIPHATIC COMPOUNDS						AROMATIC COMPOUNDS	
	ACETYLENE POLYMERS	NITRILE POLYMERS				ALIPHATIC COPOLYMERS	PAH POLYMERS	NITRILE AROMATIC POLYMERS
1 (99 Da. - 110 Da.) Peak at 103 Da.		104 ($C_4N_4^+$)	100 ($C_6N_2^+$)	105 ($C_5H_3N_3^+$)	98-101 (C_7N^+)	103 ($C_5H_3N^+$)	103 ($C_8H_7^+$)	104 ($C_7H_6N^+$)
2 (111 Da. - 122 Da.) Peak at 117 Da.	122 ($C_{10}H_2^+$)		112 ($C_7N_2^+$)		110-112 (C_8N^+)		117 ($C_9H_9^+$)	
3 (123 Da. - 134 Da.) Peak at 127 Da.		130 ($C_5N_5^+$)	124 ($C_8N_2^+$)	131 ($C_6H_3N_4^+$)	122-124 (C_9N^+)	129 ($C_7H_5N^+$)	128 ($C_{10}H_8^+$)	129-130 ($C_9H_{7-8}N^+$)
4 (135 Da. - 147 Da.) Peak at 141 Da.	146 ($C_{12}H_2^+$)		136 ($C_9N_2^+$)		134-136 146-148 ($C_{10-11}N^+$)		141 ($C_{11}H_9^+$)	
5 (148 Da. - 158 Da.) Peak at 153 Da.		156 ($C_6N_6^+$)	148 ($C_{10}N_2^+$)	157 ($C_7H_3N_5^+$)		155 ($C_9H_7N^+$)	153 ($C_{12}H_9^+$)	156 ($C_{11}H_{10}N^+$)
6 (159 Da. - 169 Da.) Peak at 165 Da.	170 ($C_{14}H_2^+$)		160 ($C_{11}N_2^+$)		158-160 ($C_{12}N^+$)		165 ($C_{13}H_9^+$)	

LEGEND				
Percent compared to group probability	0% - 12%	13% - 24%	25% - 36%	37% - 48%

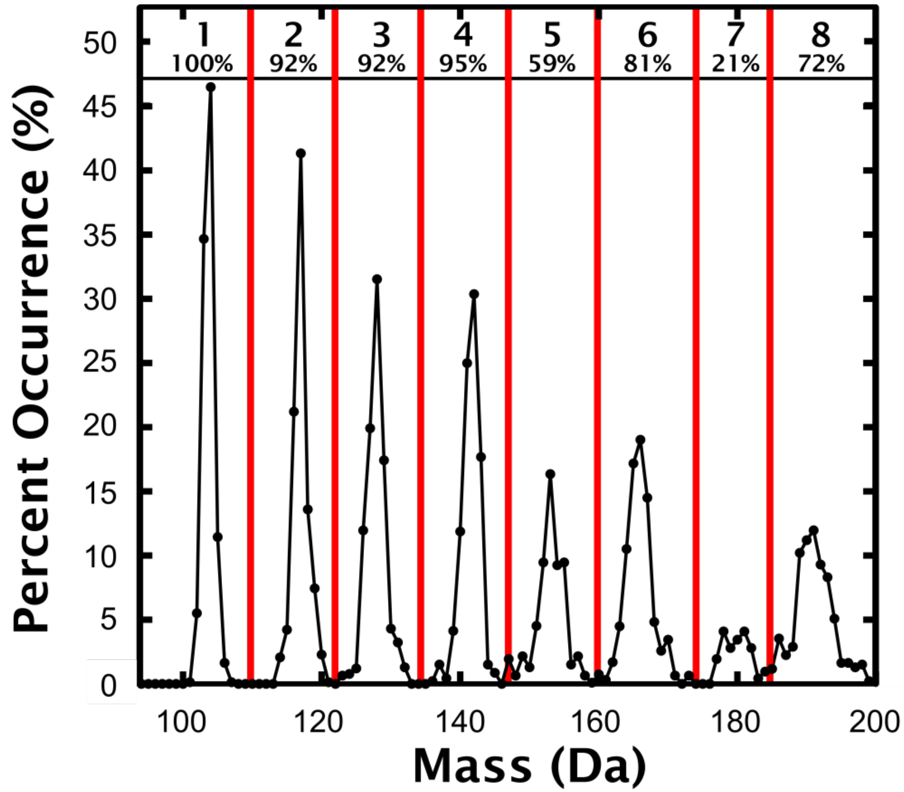
Aromatic Chemistry

- The Most likely components of the high mass ions are **aromatic compounds**
- Chemistry from *Wilson and Atreya (2003)*

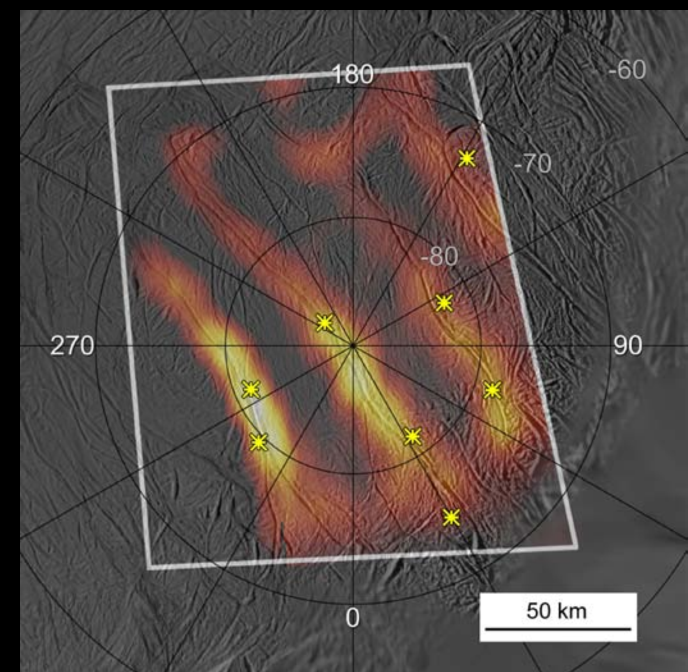
Percent Occurrence

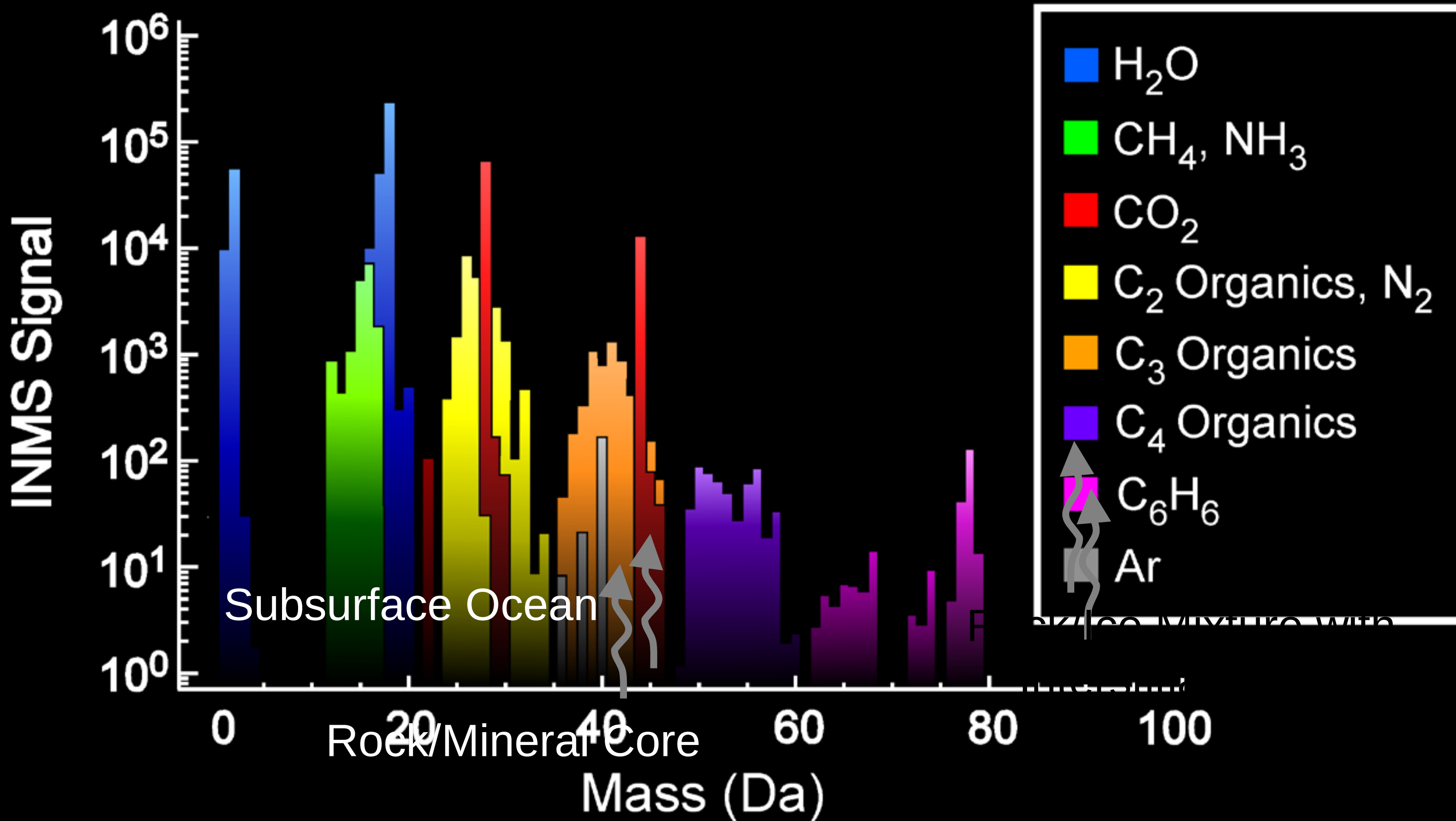
- The likelihood of a peak in the mass per charge spectrum occurring at the specified mass bin.
- Peaks occur every **12-14 Da.**

Crary et al. (2009)

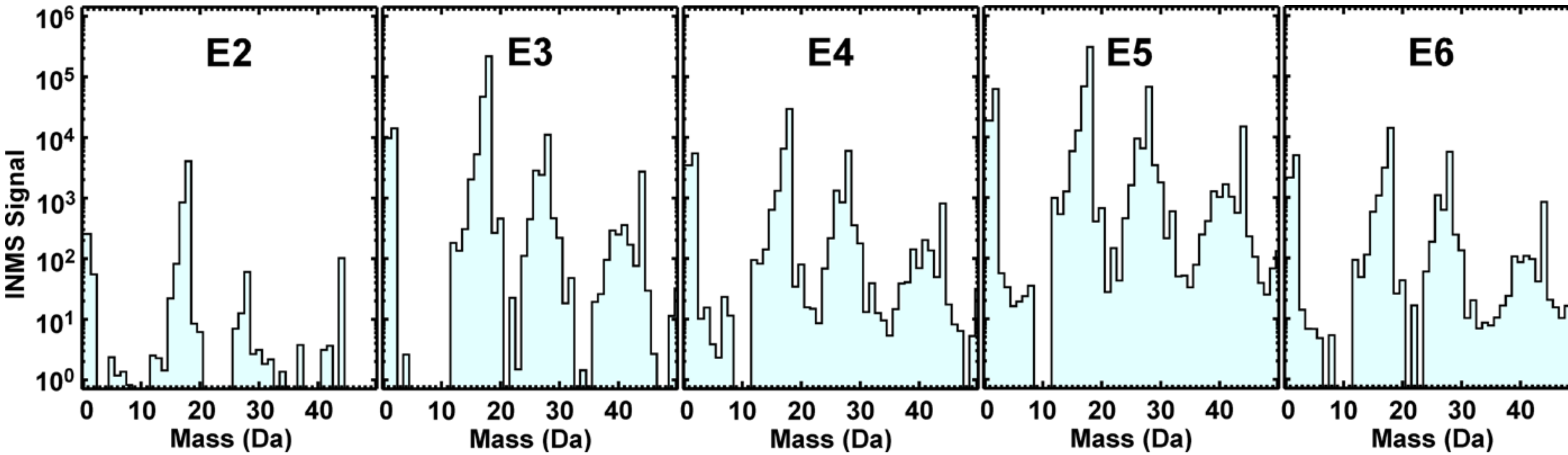


INMS observations of the icy moon Enceladus



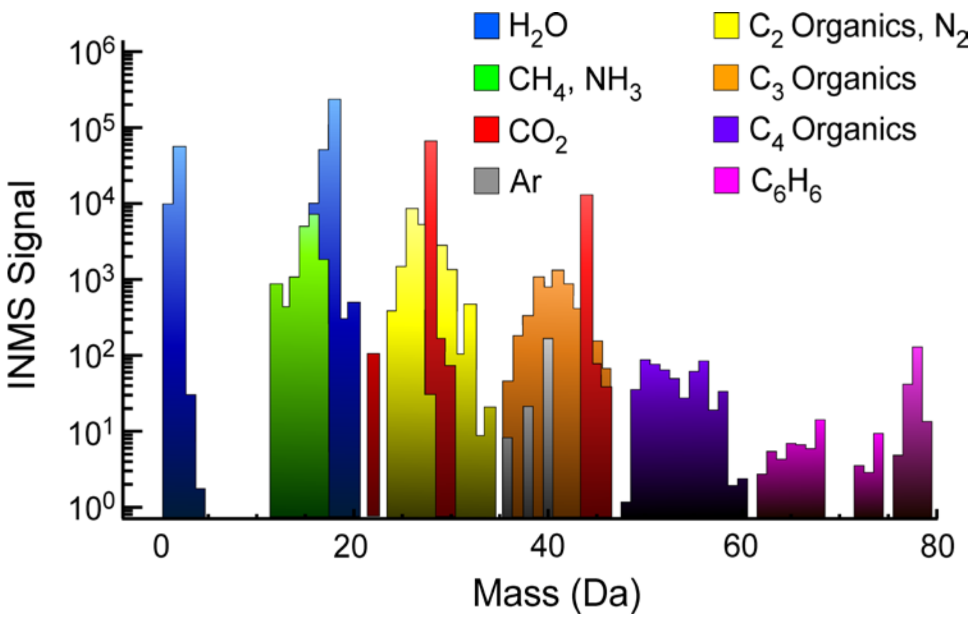


Subsurface Chemistry



Encounter	Avg. Speed wrt Enceladus	Minimum distance to South Polar hotspot	Ram Angle at time of Plume Max
E2	8.184 km/s	330 km	57 deg.
E3	14.41 km/s	242 km	0 deg.
E4	17.72 km/s	193 km	80 deg.
E5	17.73 km/s	167 km	0 deg.
E6	17.71 km/s	310 km	73 deg.

Enceladus' plume is composed primarily of water vapor with carbon dioxide, methane, ammonia, ^{40}Ar, and a host of organics.



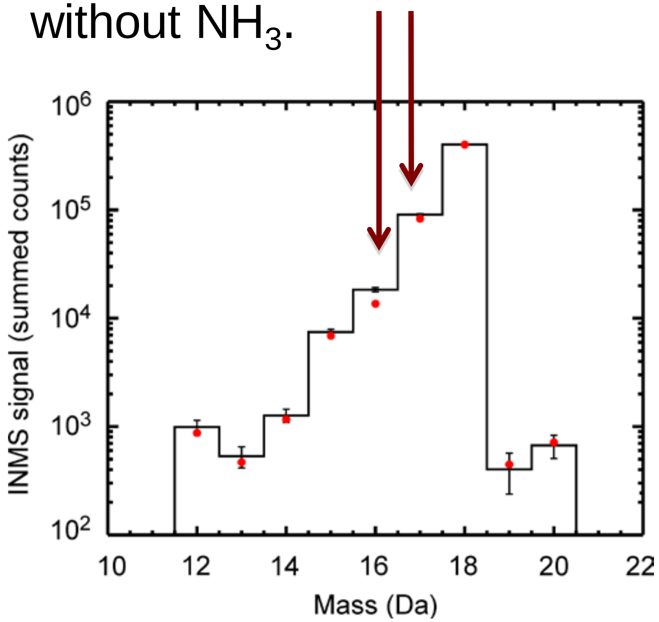
Waite et al. (2009)

Table 1 | INMS determination of plume composition on 9 October 2008

Species	Volume mixing ratio
H_2O	0.90 ± 0.01
CO_2	0.053 ± 0.001
CO	[0.044]
H_2	[0.39]
H_2CO	$(3.1 \pm 1) \times 10^{-3}$
CH_3OH	$(1.5 \pm 0.6) \times 10^{-4}$
C_2H_4O	$< 7.0 \times 10^{-4}$
C_2H_6O	$< 3.0 \times 10^{-4}$
H_2S	$(2.1 \pm 1) \times 10^{-5}$
^{40}Ar	$(3.1 \pm 0.3) \times 10^{-4}$
NH_3	$(8.2 \pm 0.2) \times 10^{-3}$
N_2	< 0.011
$HCN^{\dagger}$	$< 7.4 \times 10^{-3}$
CH_4	$(9.1 \pm 0.5) \times 10^{-3}$
C_2H_2	$(3.3 \pm 2) \times 10^{-3}$
C_2H_4	< 0.012
C_2H_6	$< 1.7 \times 10^{-3}$
C_3H_4	$< 1.1 \times 10^{-4}$
C_3H_6	$(1.4 \pm 0.3) \times 10^{-3}$
C_3H_8	$< 1.4 \times 10^{-3}$
C_4H_2	$(3.7 \pm 0.8) \times 10^{-5}$
C_4H_4	$(1.5 \pm 0.6) \times 10^{-5}$
C_4H_6	$(5.7 \pm 3) \times 10^{-5}$
C_4H_8	$(2.3 \pm 0.3) \times 10^{-4}$
C_4H_{10}	$< 7.2 \times 10^{-4}$
C_5H_6	$< 2.7 \times 10^{-6}$
C_5H_{12}	$< 6.2 \times 10^{-5}$
C_6H_6	$(8.1 \pm 1) \times 10^{-5}$

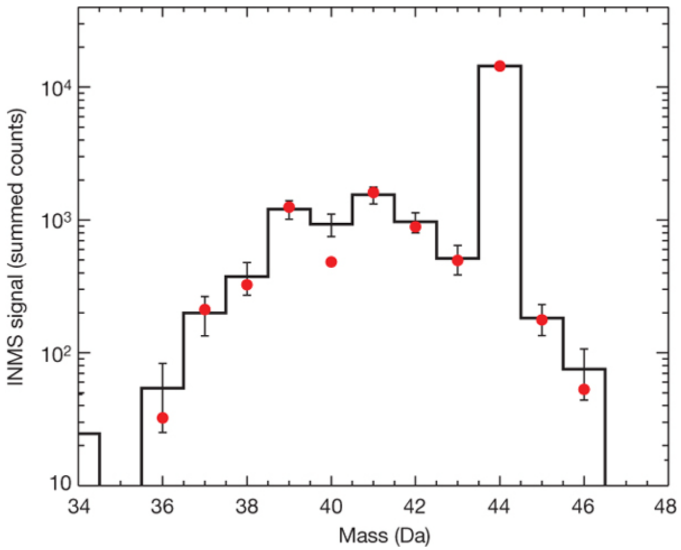
Ammonia at Enceladus

INMS data taken at Enceladus requires that NH_3 provide significant signal at masses 16 and 17 Da. Model mixture discrepancy stands at ~3 sigma without NH_3.



- NH_3, together with CH_3OH and salts, permits existence of liquid water down to as low as 176 K.
- Preservation of oceanic layer would maintain conditions necessary for renewed episodes of tidal heating and geological activity. (Roberts and Nimmo)
- Low upper limit of primordial Ar suggests NH_3, rather than clathrate, is major carrier of N in the material that formed Enceladus

^{40}Ar: Water – Rock Interactions



^{40}Ar fills the residual signal at 40 Da that cannot be accounted for by other species detected by the INMS at Enceladus.

$^{40}K \longrightarrow {}^{40}Ar$ ($t_{1/2}$ = 1.25 billion yr)

INMS observes more ^{40}Ar than would be expected from the available K in Enceladus' rock

Pure Ice: No mechanism for concentration or leeching

Water + Ice: No mechanism for leeching

Water + Ice + Rock: Leeching through water-rock interactions and concentration within the water

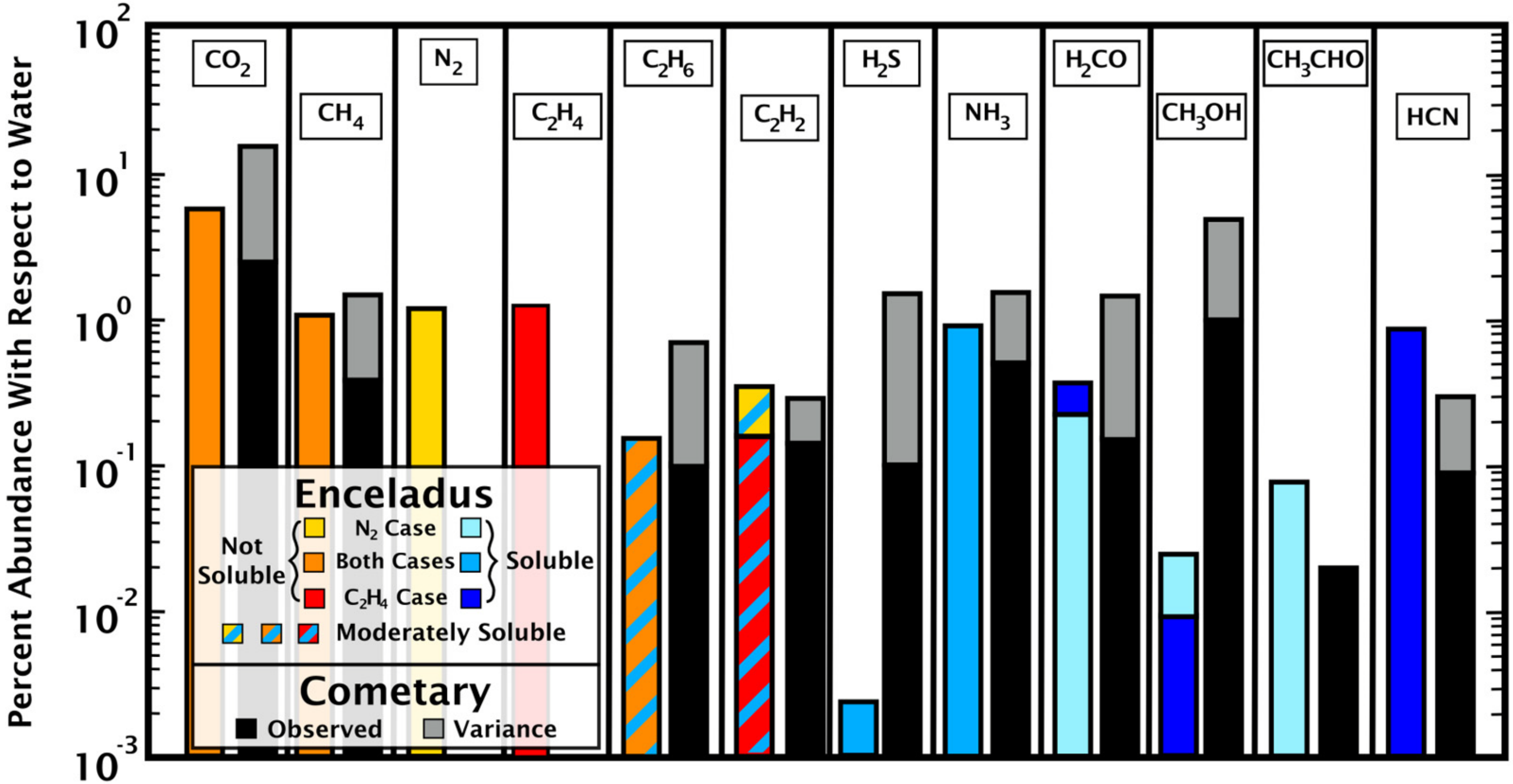
- Plume could also access degassing clathrate hydrate formed from ^{40}Ar-enriched ocean
- ^{40}Ar observed by INMS either not steady-state or plume activity is intermittent (<1% duty cycle)

Notable Ambiguities: CO and C_2H_4 vs. N_2 + HCN

- CO in Enceladus plume cannot be separated from that produced via impact dissociation of CO_2 (a limit of CO + CO_2 = 5.4%)
- Deficiency of CO relative to comets means CO may not have been present in large quantities in the icy planetesimals or may have been hydrothermally processed

- Analysis of INMS data shows that either C_2H_4 and/or a combination of N_2 and HCN are present
- C_2H_4 is not seen in comets and unlikely to be present in large quantities in icy planetesimals
- Presence of N_2 explainable by hydrothermal processing of NH_3
- HCN rapidly hydrolyzes to formic acid and NH_3 in warm water
- Coexistence of N_2 and HCN would promote the idea of plume consisting of mixture of materials from sources experiencing different degrees of aqueous processing

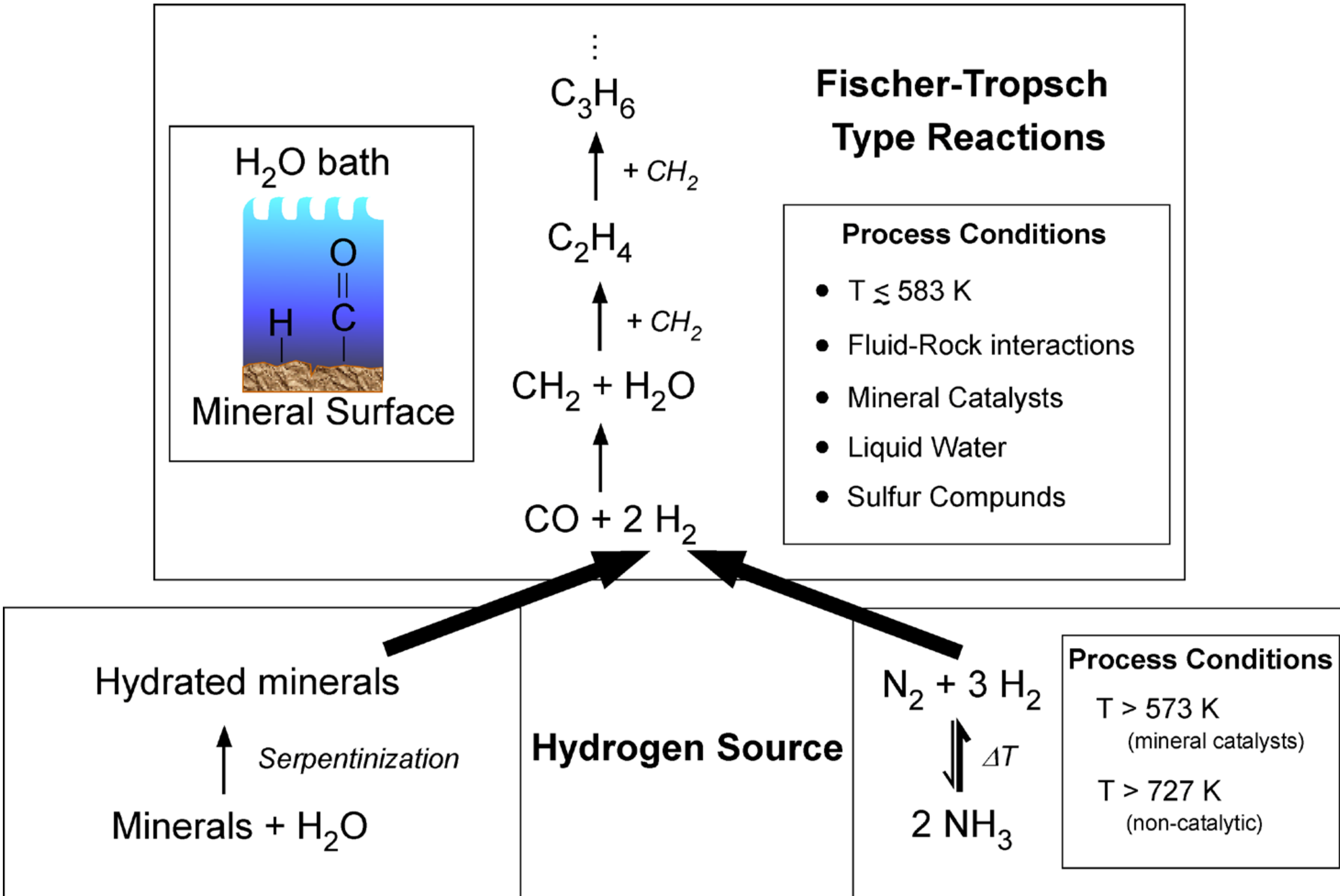
Enceladus vs. Comets



	D/H	$^{18}O/^{16}O$	$^{12}C/^{13}C$
Enceladus	2.9 (+1.5/–0.7) x 10^{-4}	2.1 (+0.4/–0.2) x 10^{-3}	84 ± 13
Comets	3.1 (+0.4/–0.5) x 10^{-4} (a)	1.93 ± 0.12 x 10^{-3} (a)	90 ± 10 (b)

(a) Balsiger, H. et al. D/H and 18O/16O ratio in the hydronium ion and in neutral water from in situ ion measurements in comet Halley, *J. Geophys. Res.* **100**, 5827-5834, (1995).
(b) Wycoff, S. et al. Carbon isotope abundances in comets. *Astrophys. J.* **535**, 991-999 (2000).

Chemical Evolution of Volatiles in the Interior?



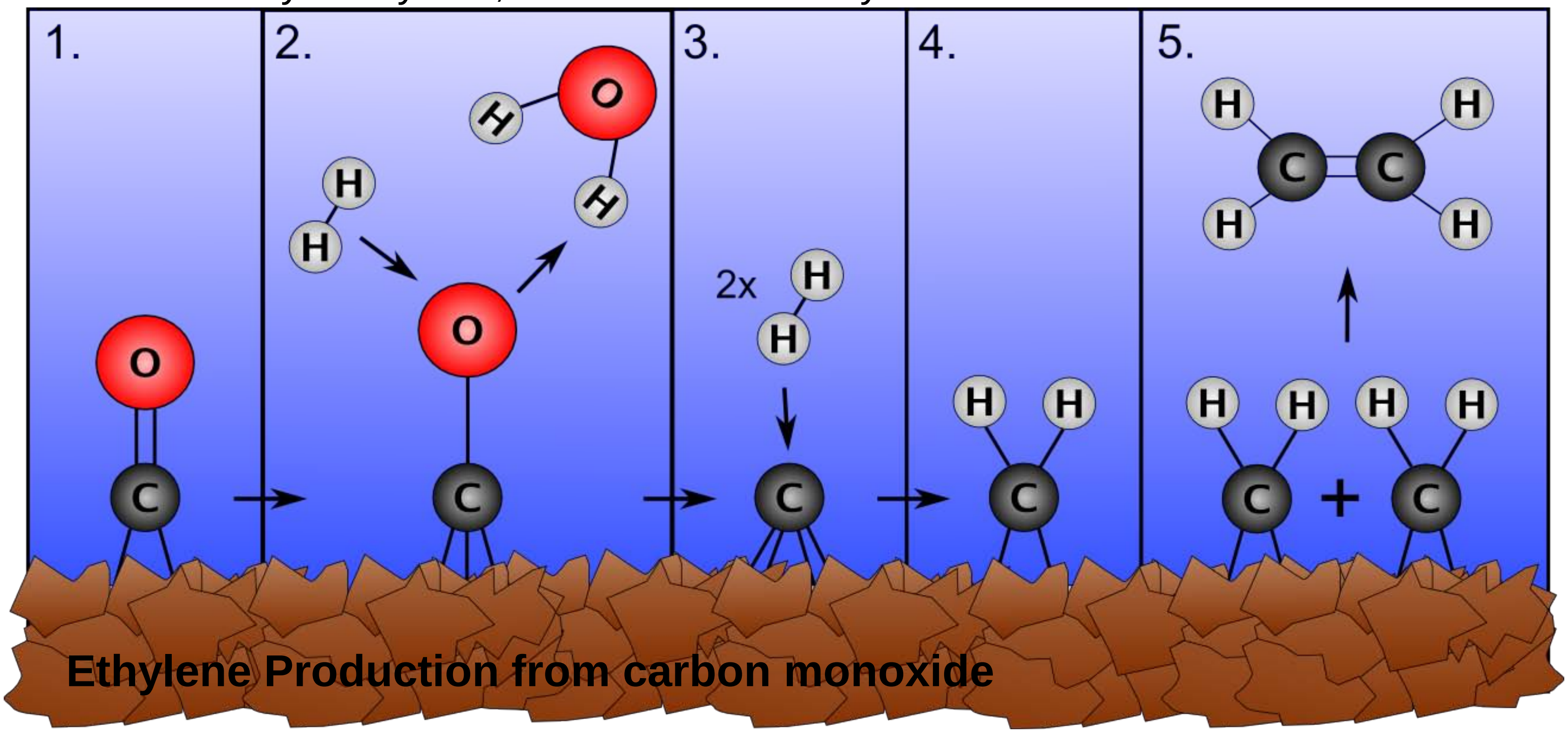
Fischer-Tropsch Synthesis

- CO or CO_2 interaction with a surface abiotically produces hydrocarbons.

$$2nCO + nH_2 \rightarrow [CH_2]_n + nCO_2$$

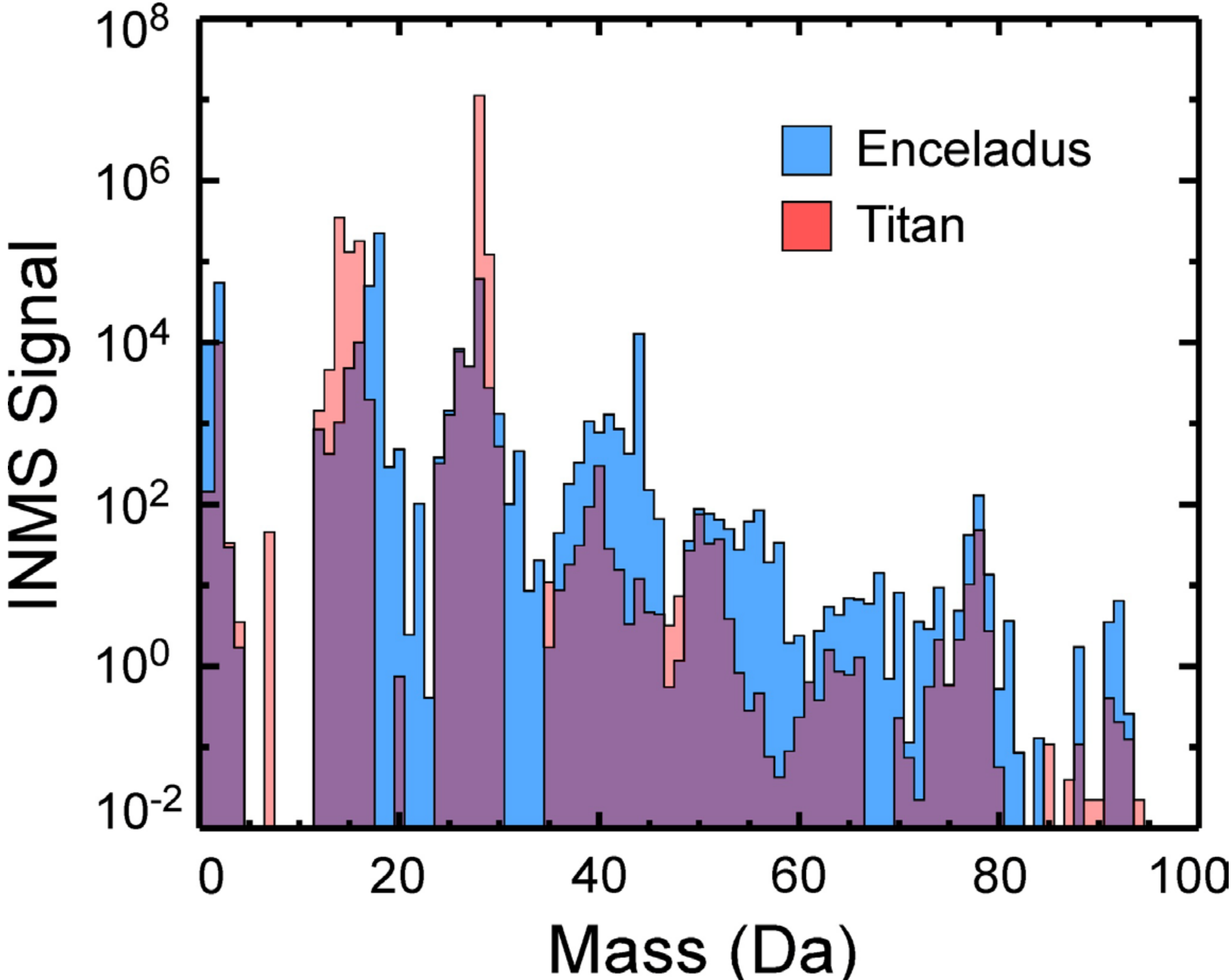
$$nCO + 2nH_2 \rightarrow [CH_2]_n + nH_2O$$

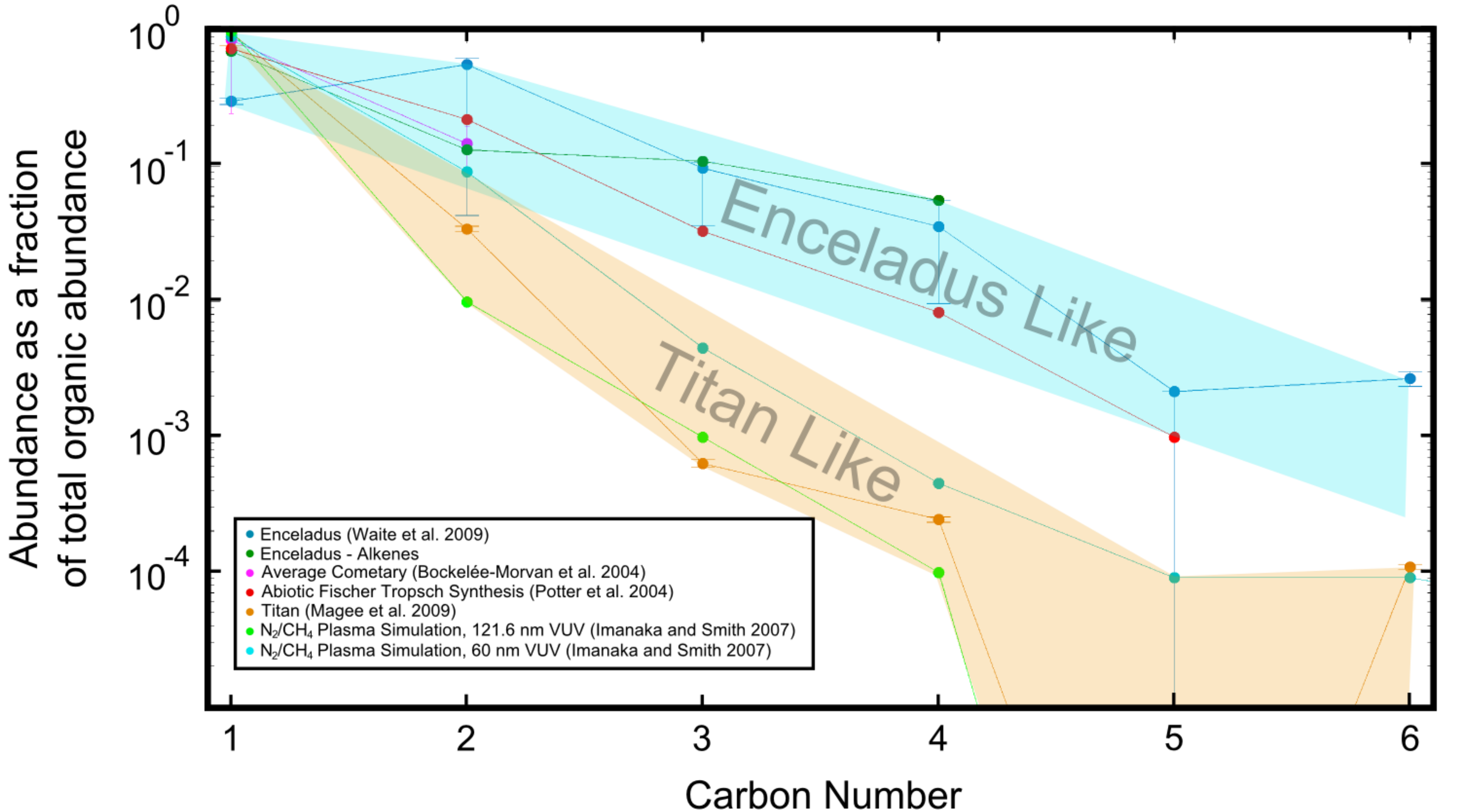
- This process is **efficient**, **highly exothermic** ($\Delta H \sim -40$ kcal/mol), and produces alkenes and alkanes. Alkene to alkane ratio is increased when potassium is present.
- The process also efficiently converts methanol (CH_3OH) and other alcohols to hydrocarbons (generally alkanes) through similar processes.
- Can be catalyzed by iron, cobalt or certain clays.



Ethylene Production from carbon monoxide

Composition Comparison, Enceladus vs. Titan



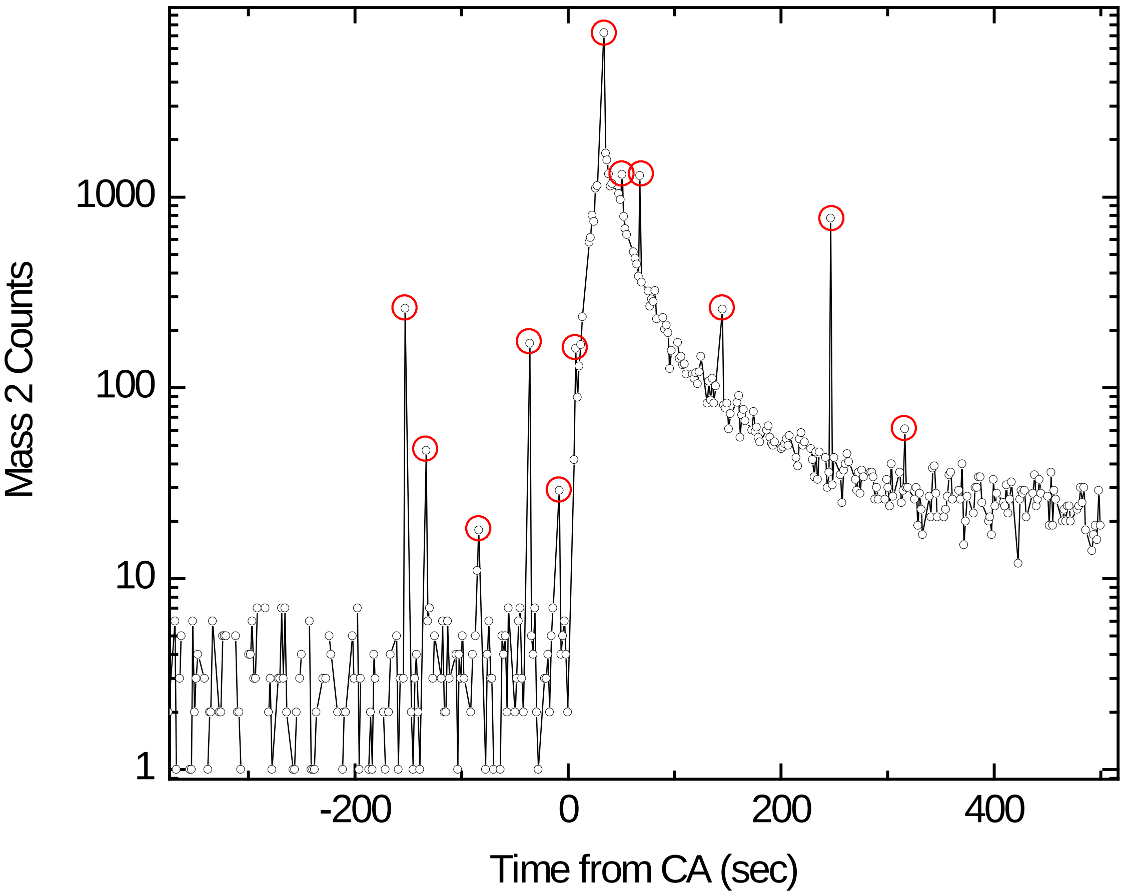


- **Enceladus Like:** Fischer-Tropsch Synthesis type carbon distribution
- **Titan Like:** Gaseous photochemistry and ion-neutral chemistry type carbon distribution

Elemental Abundance Comparison

Element	Titan 1050 km (Cassini-INMS)	Enceladus Plume (Cassini-INMS)	Comet (Comets II)
H	4.6%	63-64%	54-65%
C	1.2%	3.2-3.7%	1.6-11%
N	94%	0.26-1.2%	0.12-0.46%
O	n.m.	32-33%	34%
S	n.m.	7×10^{-6}	0.24-0.59%
Ar	6×10^{-6}	1×10^{-4}	n.m.

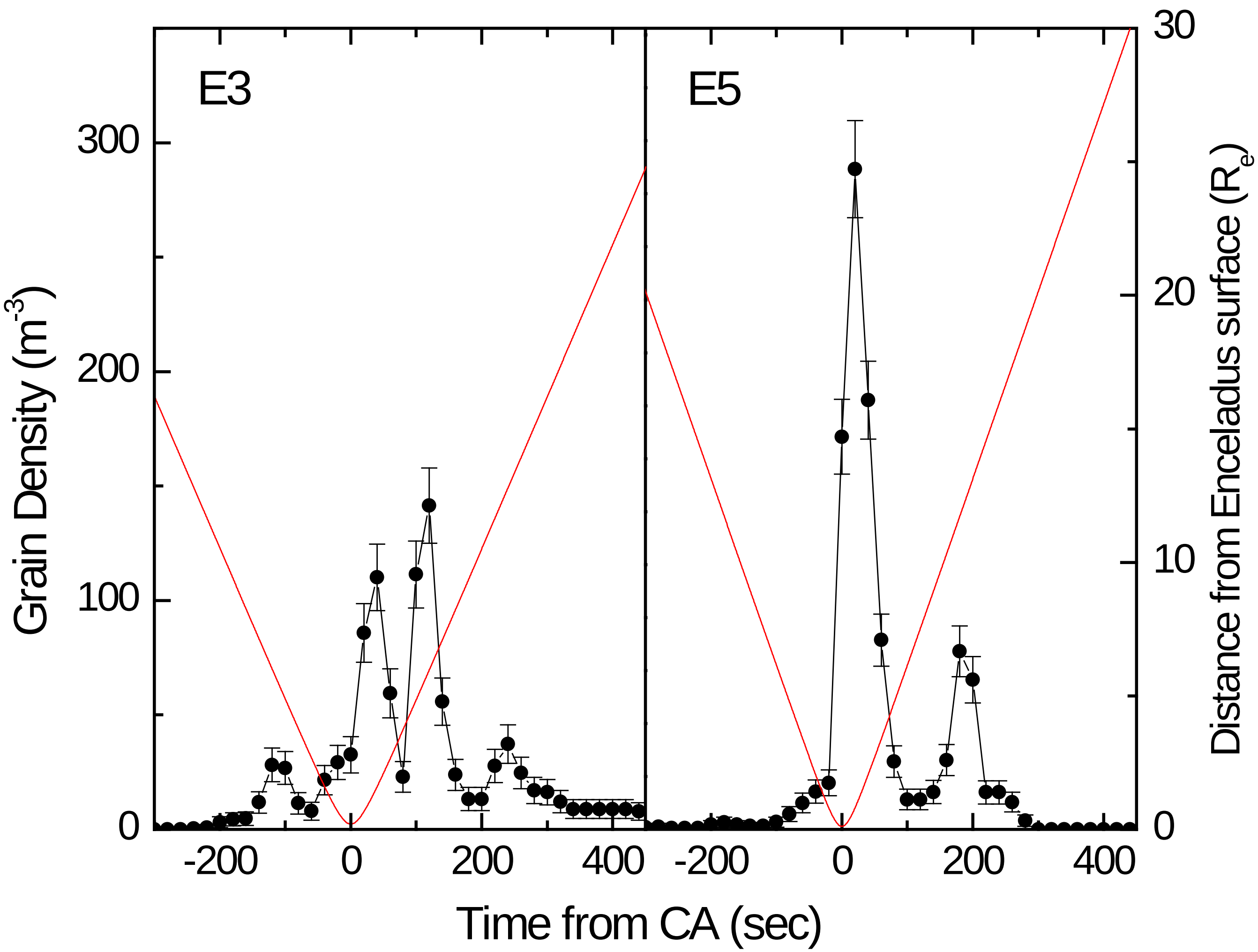
INMS detection of ice grains at Enceladus



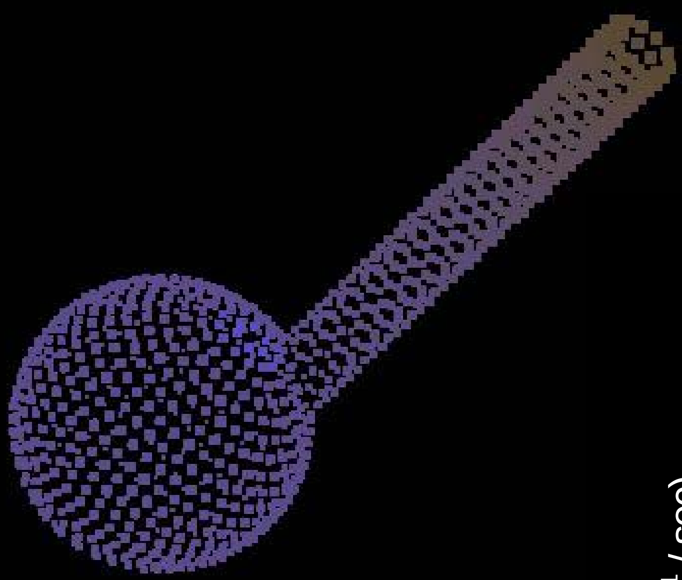
INMS data taken during Enceladus observations frequently display sudden spikes in the signal observed for a number of mass channels indicative of volatile species.

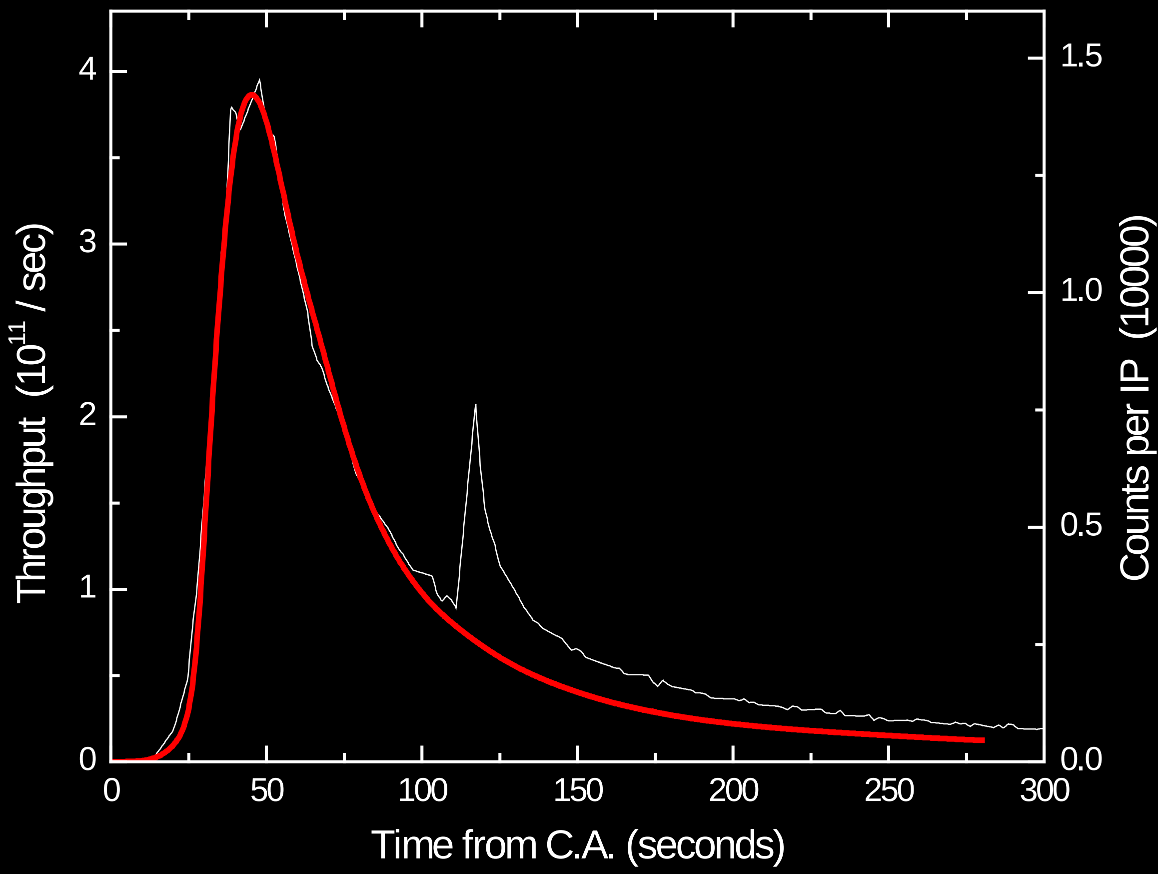
These deviations from the gas signal profile suggest the arrival of ice grains into the closed source antechamber.

Grain Jets at Encaludus - Detection by INMS

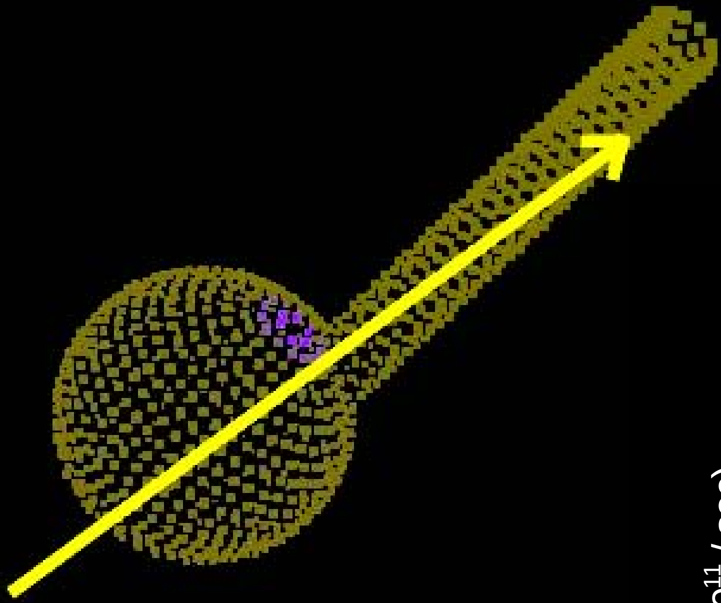


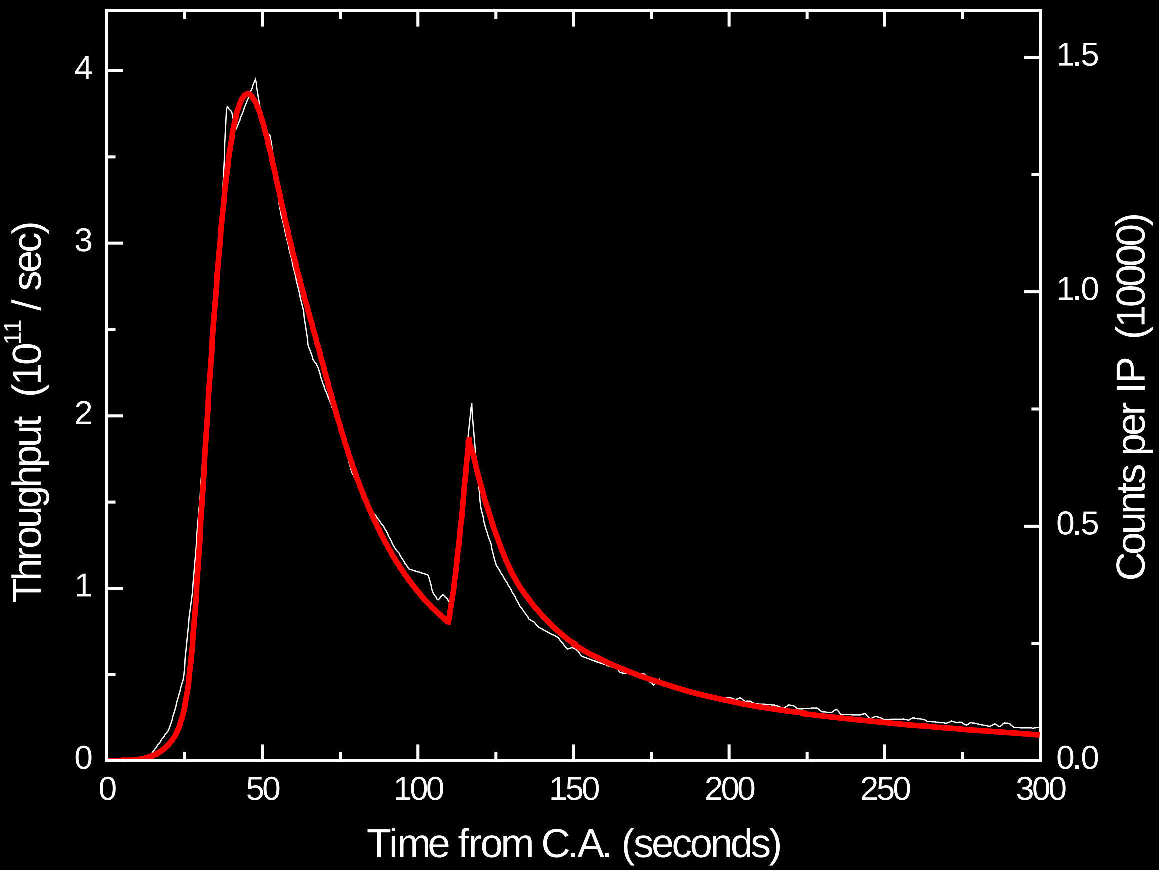
H_2O propagation to INMS detector





6um grain impact





Enceladus Plume Density: Relation to surface sources