TITAN

Ingredients for life.

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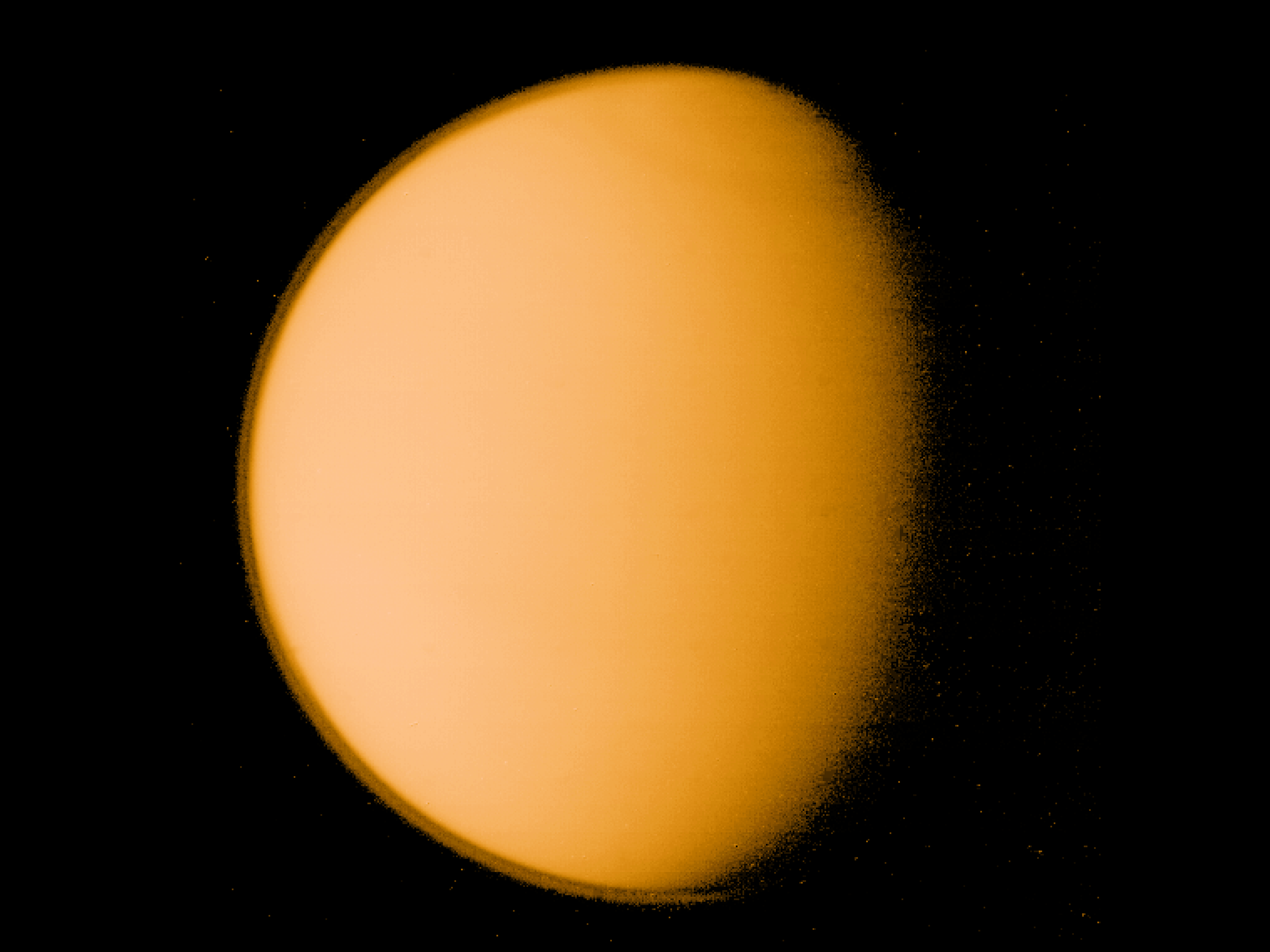
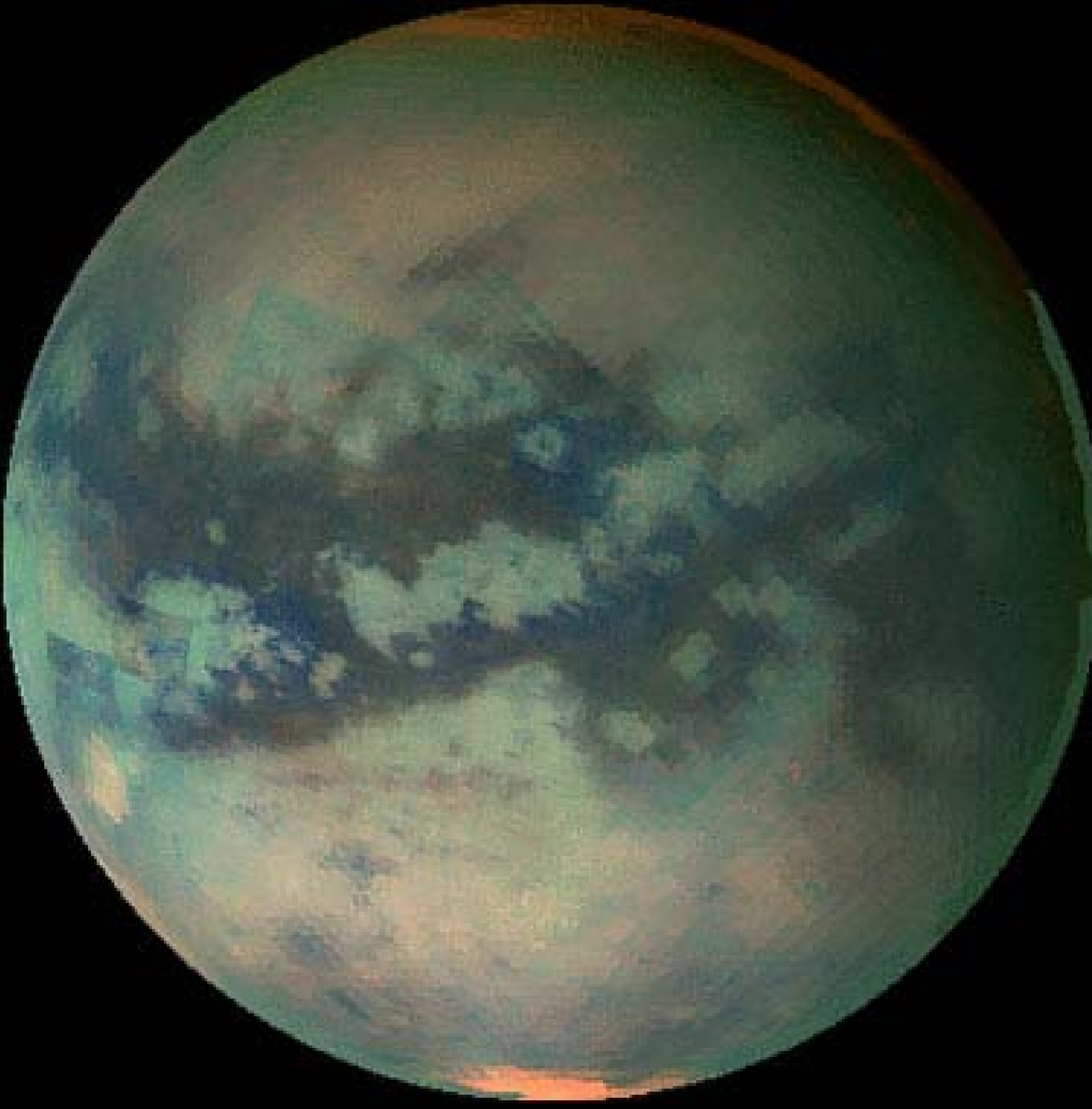
The Johns Hopkins University Applied Physics Lab

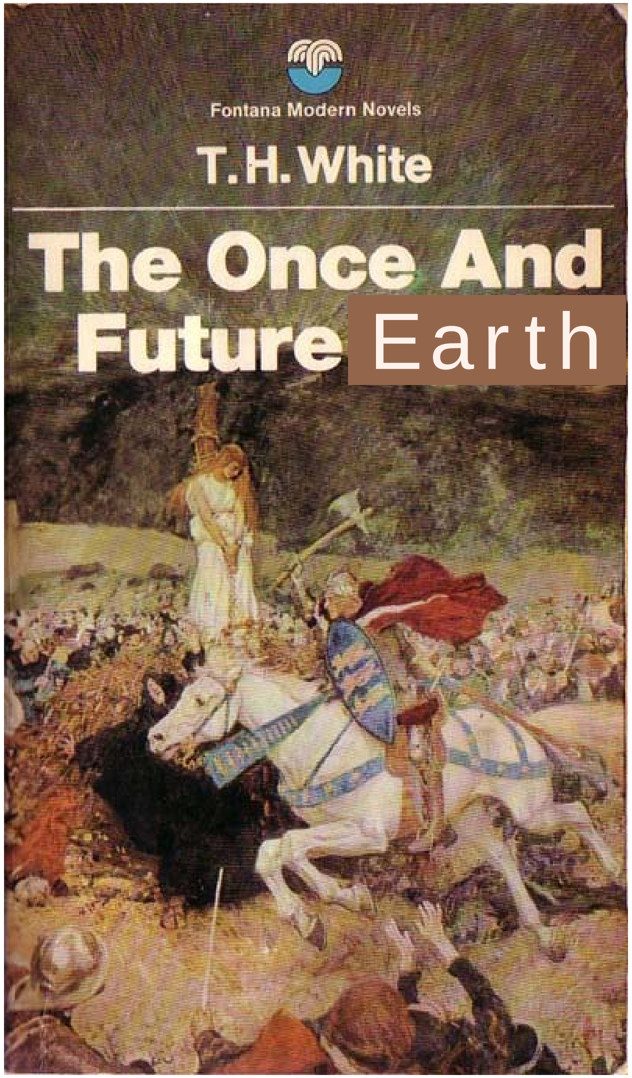
March 30, 2010





background

Titan: The once and future Earth*



Titan

Chemistry → Earth before life

Climate → Post-runaway Earth

HIC IACET
TITANUS
MUNDUS
QVONDAM
MUNDUSQVE
FVTVRVS

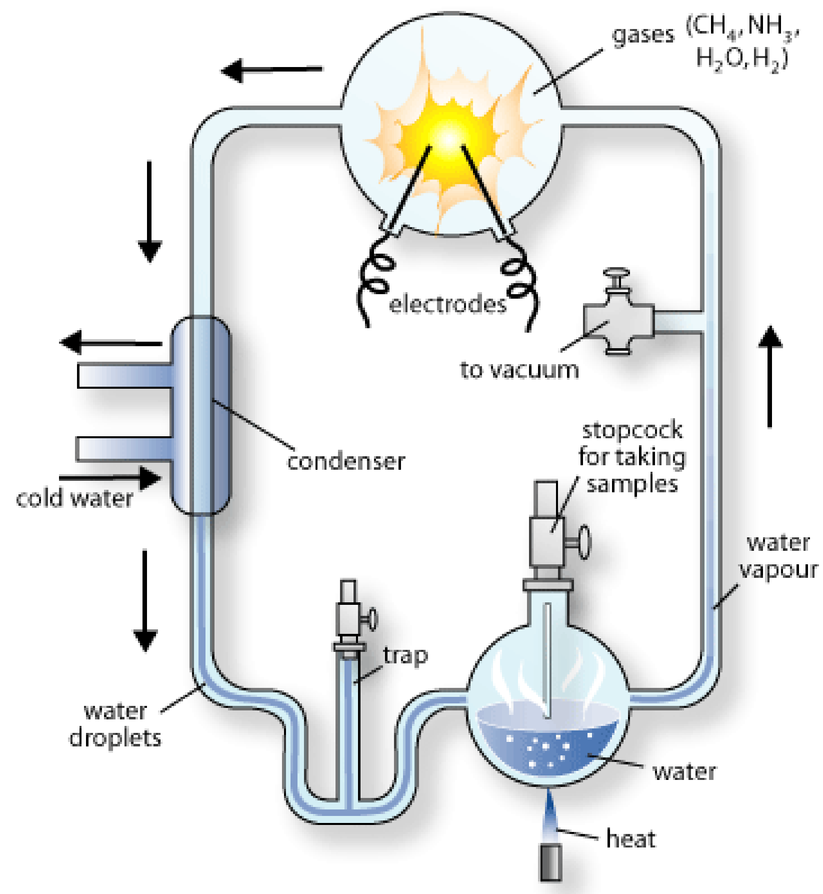
*Slide courtesy of Dr. Jonathan Lunine


Primordia
SOUP
Primordial
SOUP
O-C-O

background

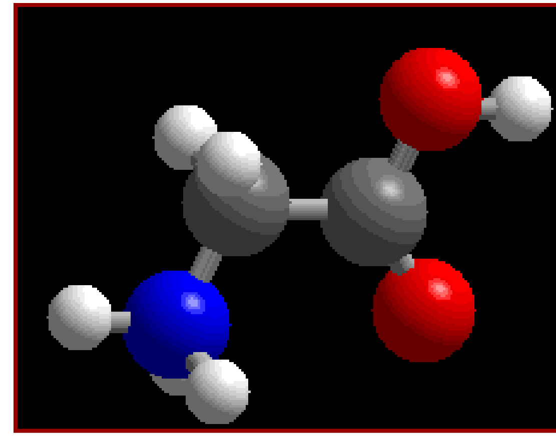
The first experiments supporting the idea that biological molecules could be produced through abiotic synthesis in an atmosphere occurred in the 1950s

- Miller (1953) showed that amino acids were formed in $CH_4/NH_3/H_2/H_2O$ rich atmospheres



Making biomolecules in Titan's atmosphere is more difficult

- (Almost) no oxygen is present there.* Oxygen is necessary for most biological molecules.



amino acid glycine

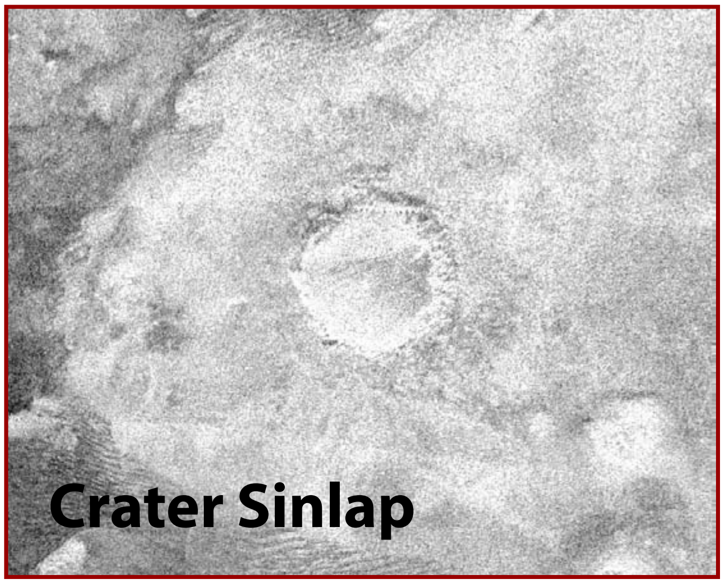
A better way to create biomolecules may involve reactions between ***simple organics*** and ***liquid water***

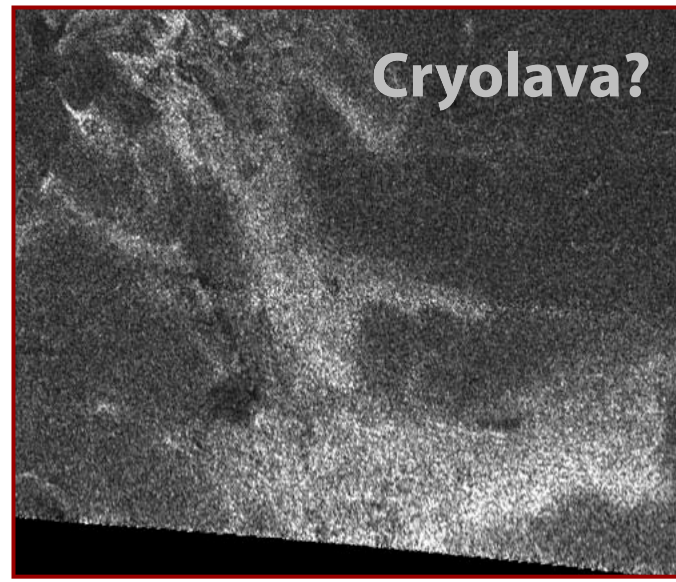
- Organics are readily hydrolyzed to produce oxidized species (Neish *et al.* 2008, 2009)

* The most abundant oxygen containing molecule, CO, is present at ~50 ppm.

How could we get liquid water on Titan?!

On average, Titan's surface is too cold for liquid water (T ~ 94 K)…





…*BUT* transient liquid water environments are created by cometary impacts and cryovolcanism (T ~ 176 – 273 K) questions

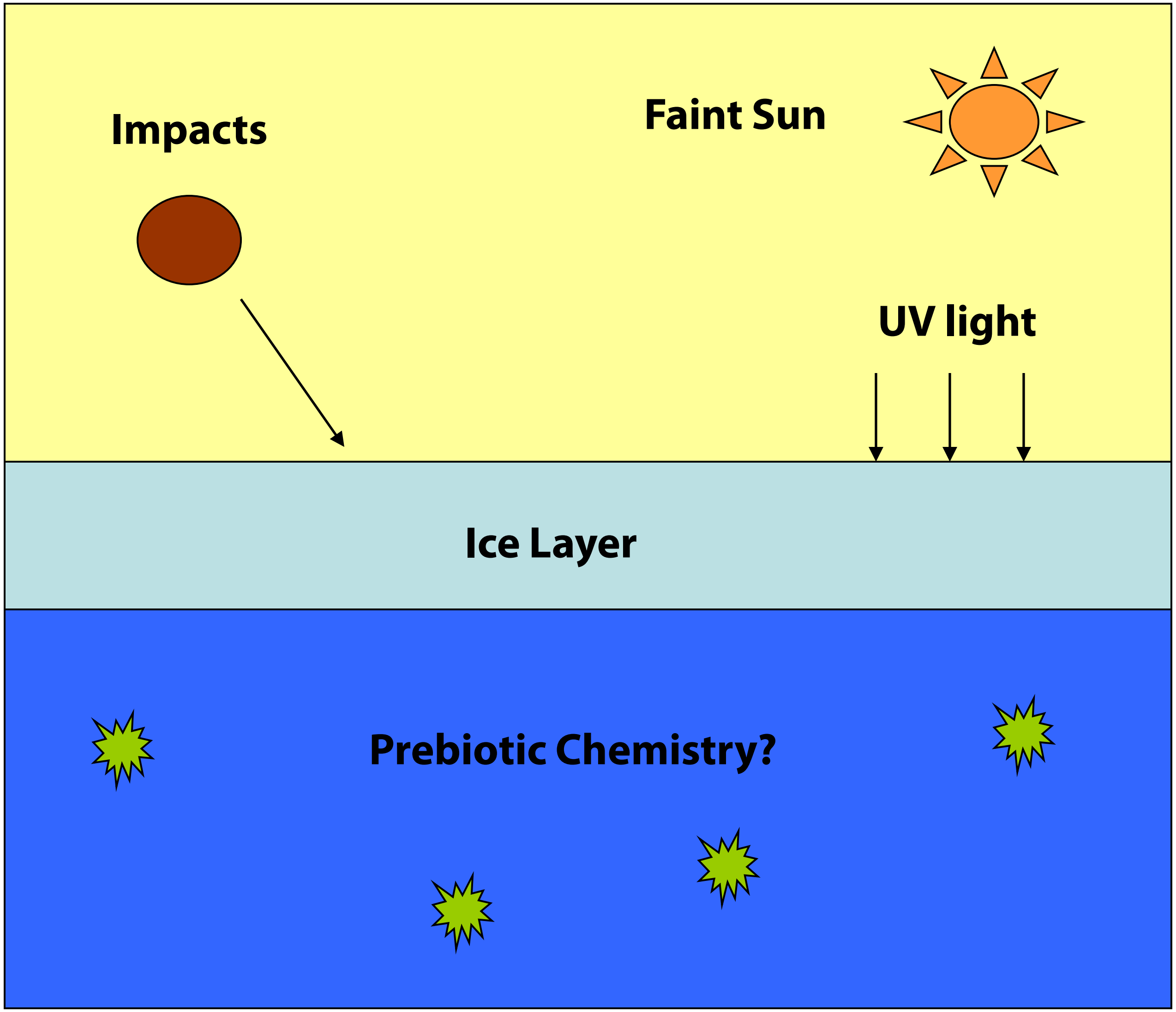
Given the transient nature of liquid water on the surface of Titan…

Are the reactions between Titan aerosols and water fast enough to produce oxygen-containing, ***prebiotic*** molecules in solidifying pools of water on Titan?

In addition…

What do these reactions tell us about possible origins of life scenarios on the early Earth (for example, the cold origin of life hypothesis)?

Cold Origin of Life:



To answer these questions, we need to determine:

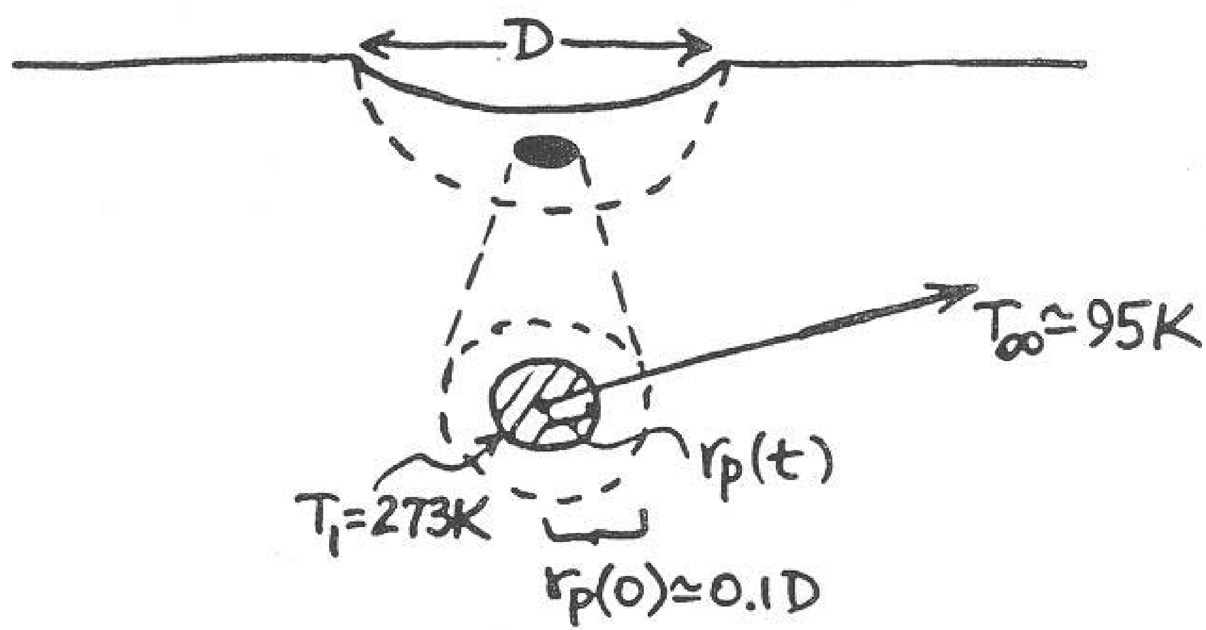
1. The freezing timescales of impact melts and cryolavas on Titan
2. The reaction rates of Titan-like organics with water at relevant temperatures
3. The nature of the resultant products

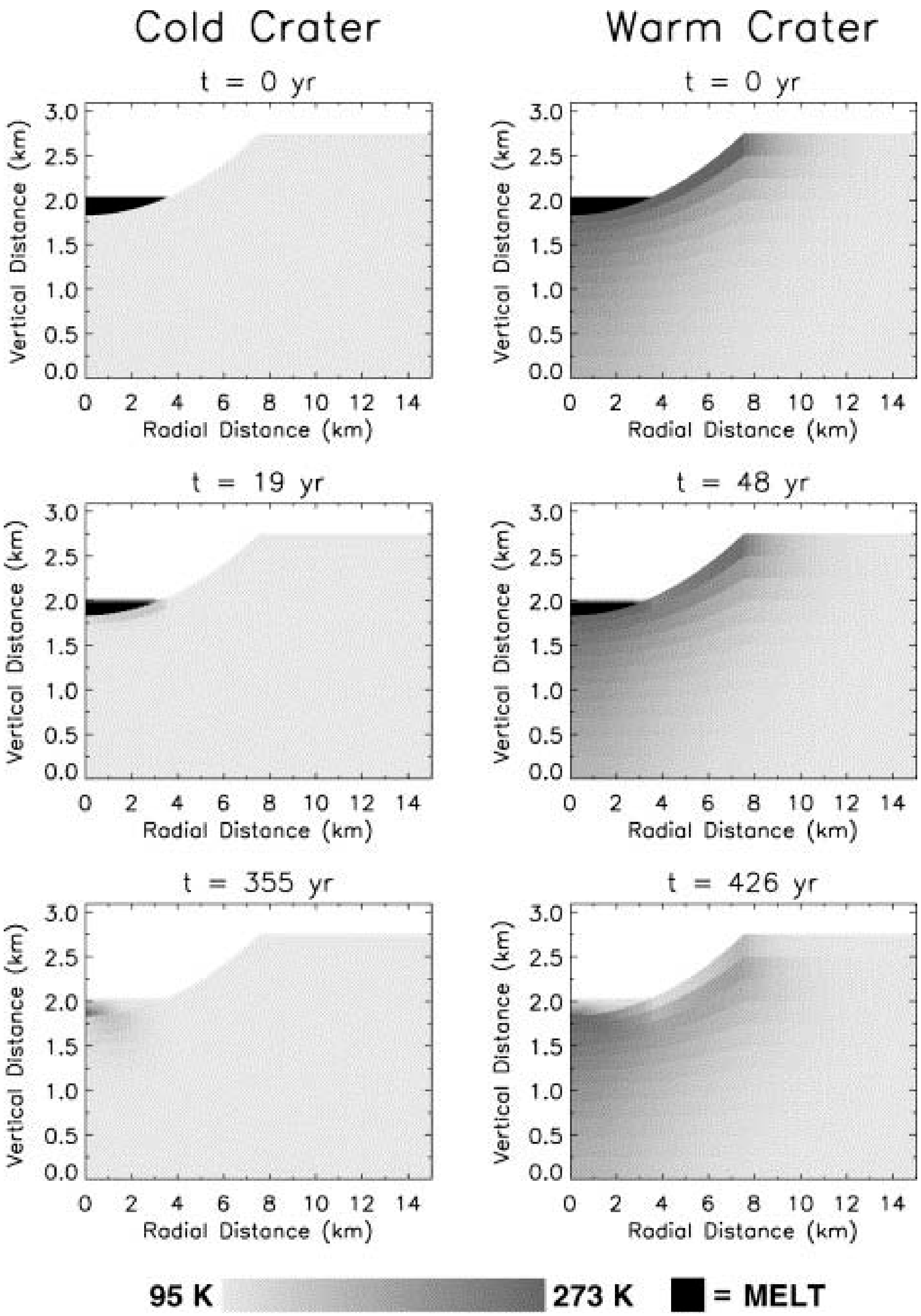
Question #1:

Freezing timescales of liquid water environments on Titan freezing timescale

Thompson and Sagan (1992) were the first to estimate the freezing timescale of impact melt pools on Titan

Using an analytic approximation, they estimated that liquid water could persist for **~10^4 yr** in a 10 km crater and for **~10^6 yr** in a 100 km crater





O'Brien et al. (2005) used a finite-difference thermal conduction code with realistic geometries and ice compositions to improve upon this initial calculation

	15 km crater	**150 km crater**
H_2O	1×10^2 – 1×10^3 yr	2×10^3 – 2×10^4 yr
$NH_3 \cdot 2H_2O$	7×10^1 – 3×10^3 yr	1×10^3 – 4×10^4 yr

Question #2:

Reaction rates of tholins in cold aqueous solutions

From Neish et al. (2008)

procedure

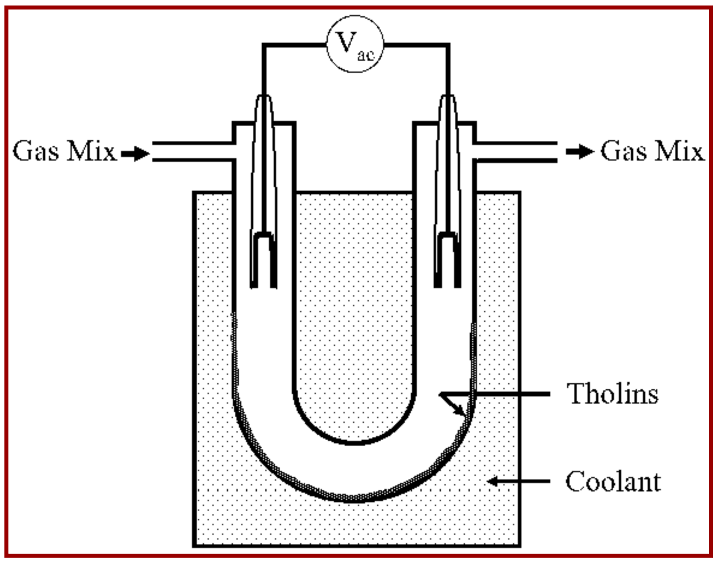
To determine the quantities of oxygen-containing organics that might be produced in aqueous solutions on Titan, we

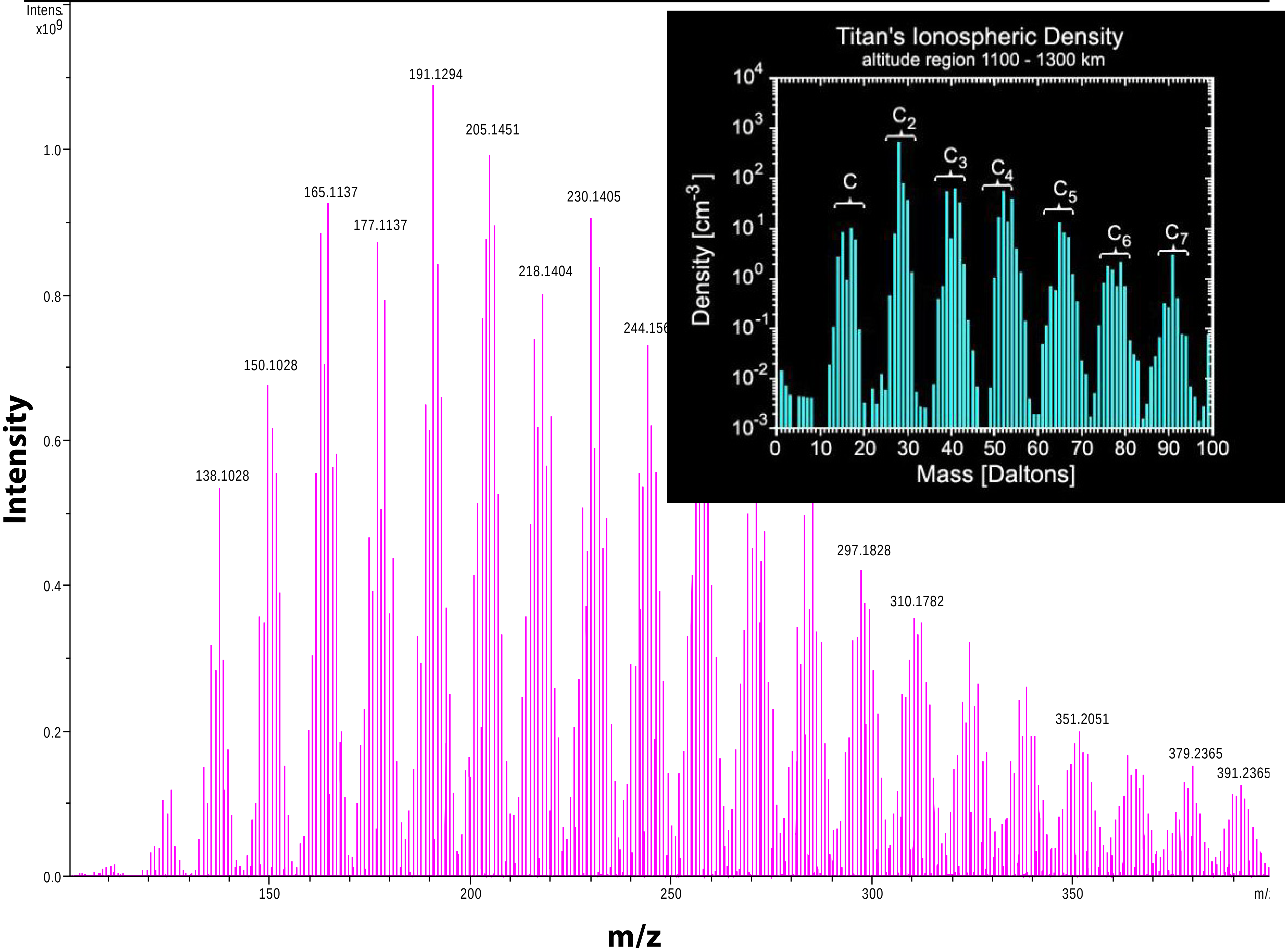
a) produced Titan analogue organic aerosols ("complex tholins")
b) determined the rates of hydrolysis of the aerosols at different temperatures
c) compared the reaction timescales to timescales for which liquid water is available on Titan

tholins

Titan analogue organic polymers ("complex tholins" or $C_xH_yN_z$) are made in the laboratory

- 2% methane in nitrogen exposed to AC electrical discharge at 5 torr and 195 K

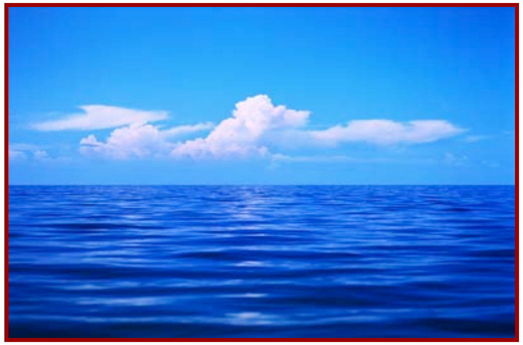


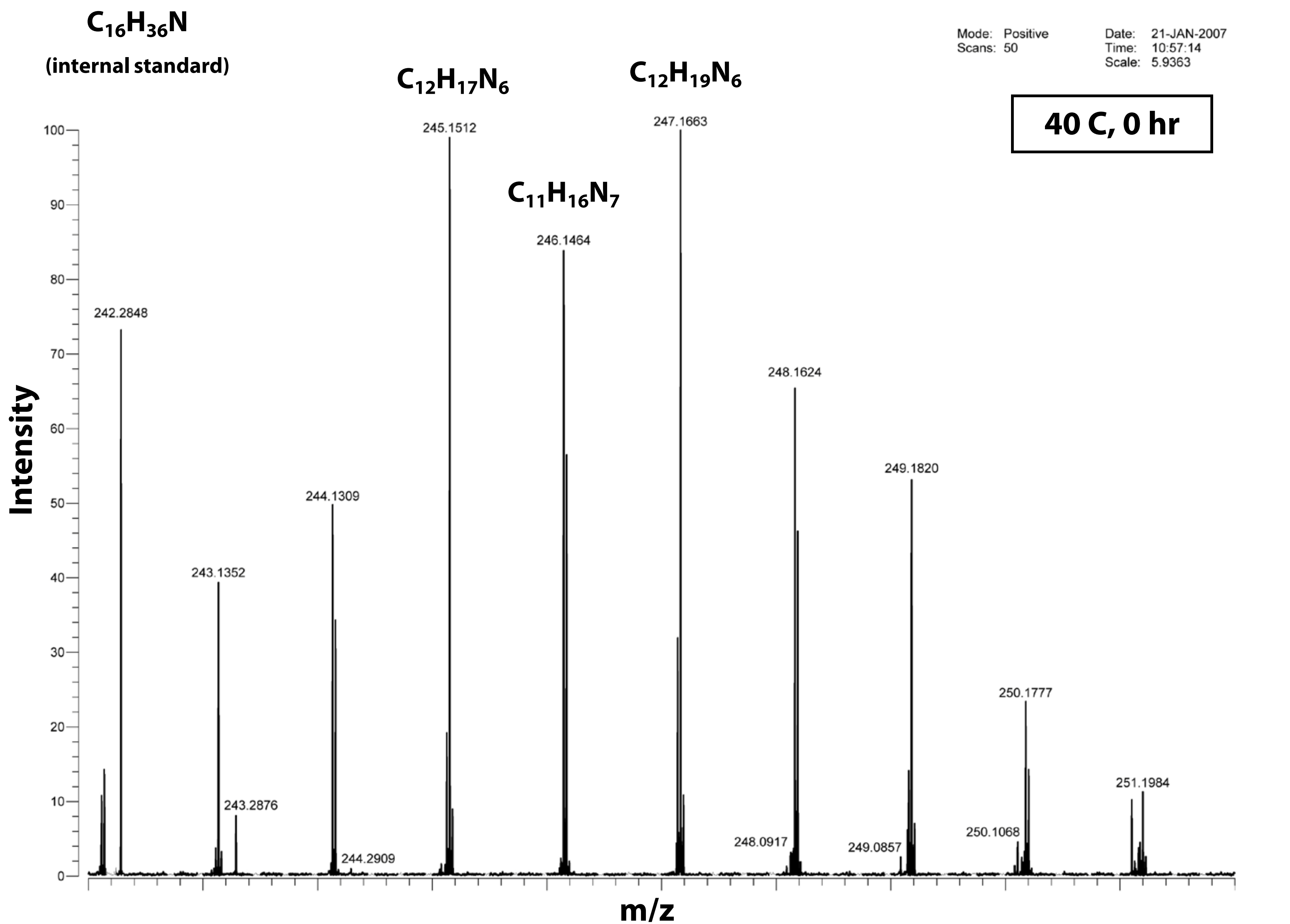

Intens.
x10^9
Intensity
m/z
138.1028
150.1028
165.1137
177.1137
191.1294
205.1451
218.1404
230.1405
244.156
297.1828
310.1782
351.2051
379.2365
391.2365
Titan's Ionospheric Density
altitude region 1100 - 1300 km
Density [cm^-3]
Mass [Daltons]
C
C2
C3
C4
C5
C6
C7

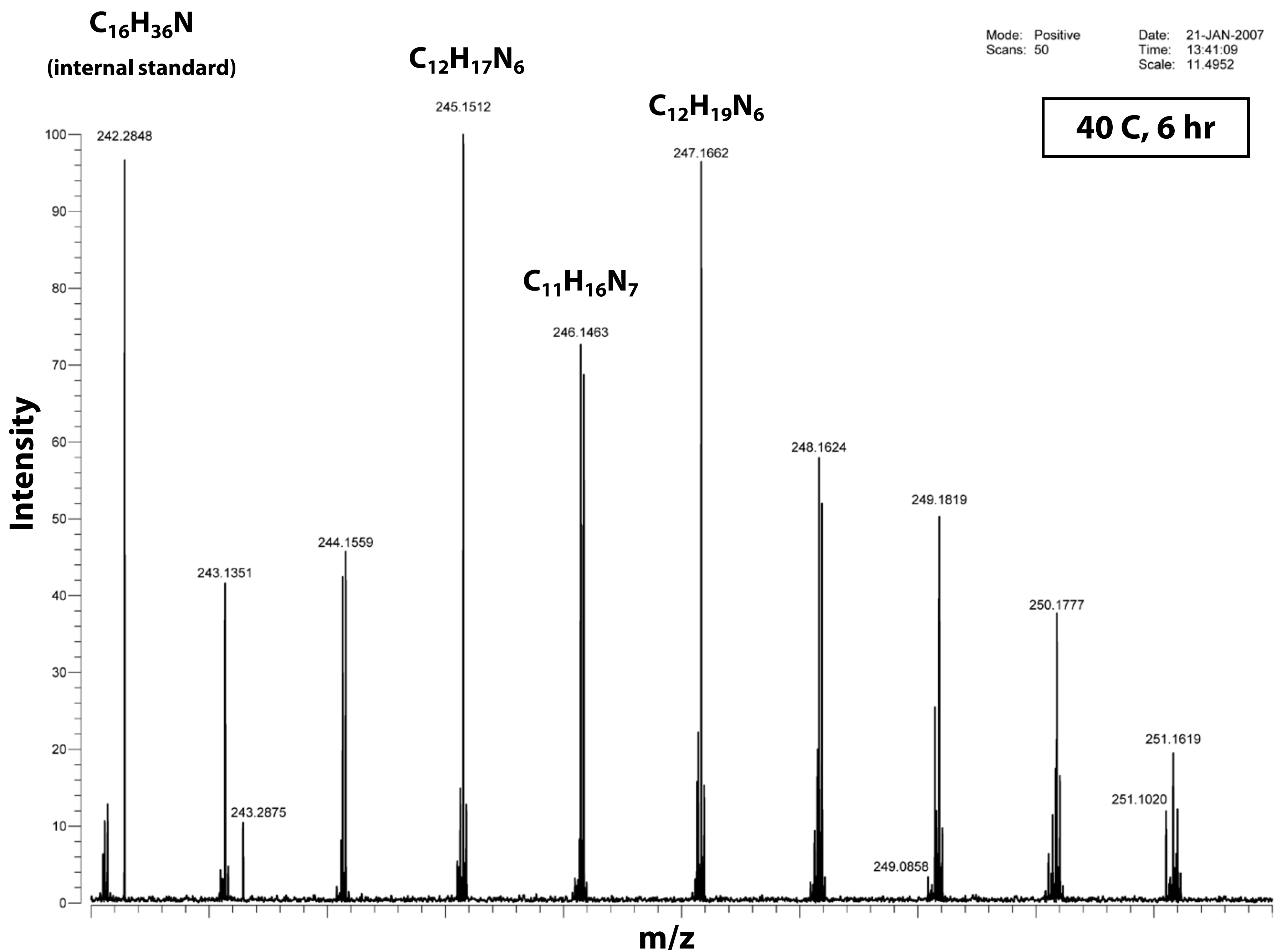
Hydrolysis study:

The organic polymers were placed in pure water at 0, 12, 24, and 40 C

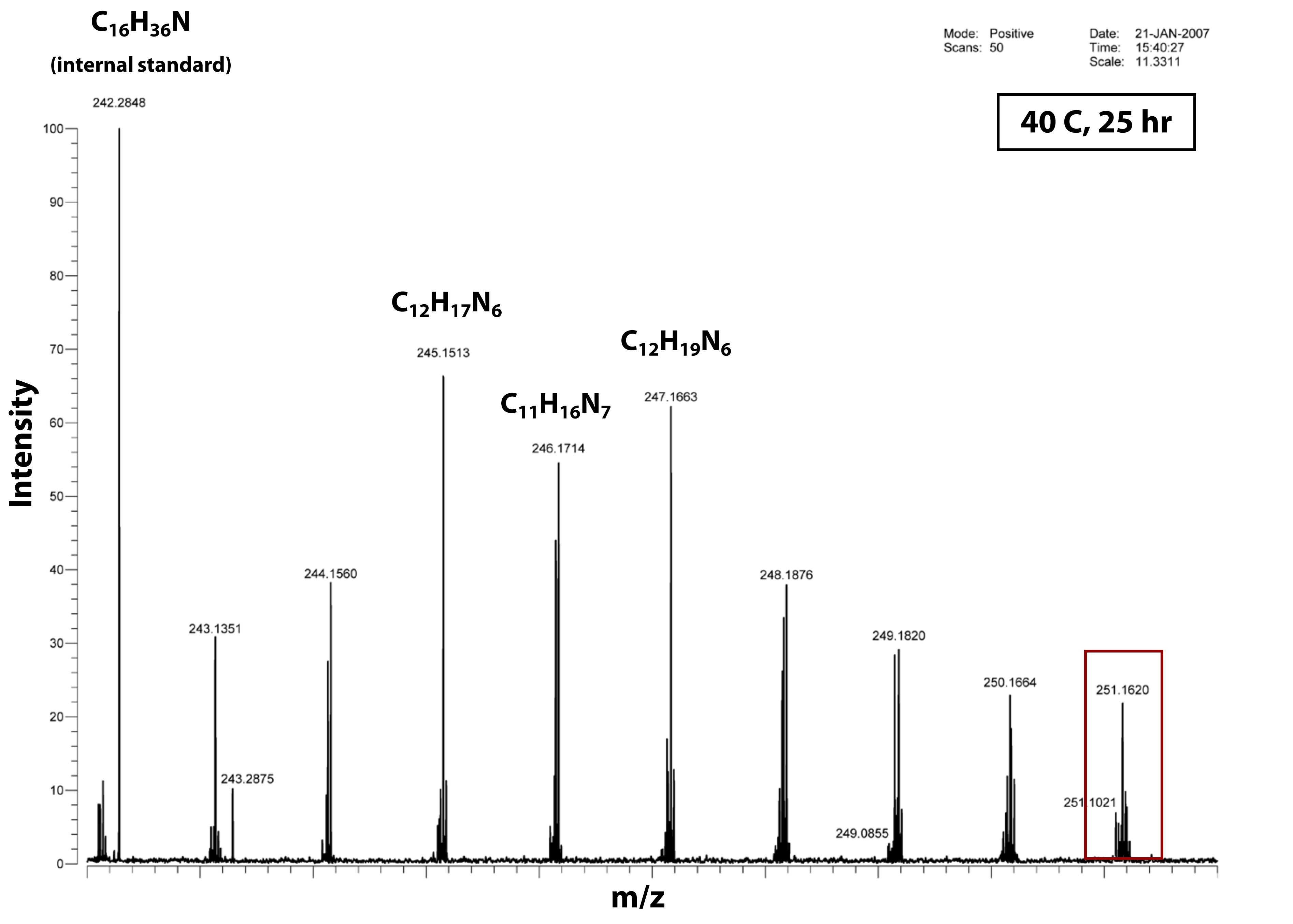
The oxidized products were monitored over time (0 – 507 h) with ultrahigh resolution FT-ICR mass spectrometry (< 0.001 amu)



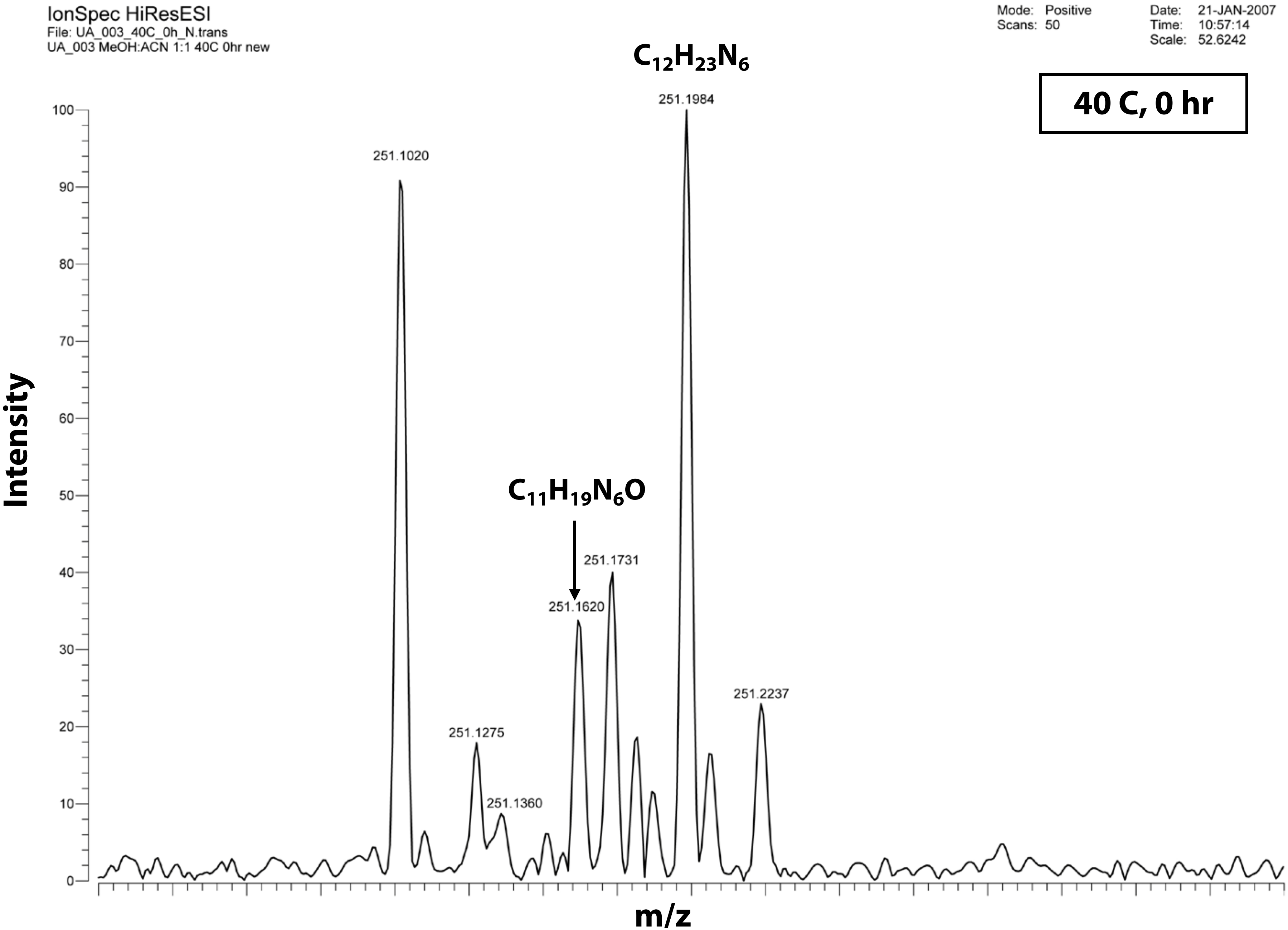

C16H36N
(internal standard)
Mode: Positive
Scans: 50
Date: 21-JAN-2007
Time: 10:57:14
Scale: 5.9363
C12H17N6
C12H19N6
40 C, 0 hr
C11H16N7
245.1512
247.1663
246.1464
242.2848
248.1624
249.1820
244.1309
243.1352
250.1777
251.1984
243.2876
244.2909
248.0917
249.0857
250.1068
Intensity
m/z
100
90
80
70
60
50
40
30
20
10
0

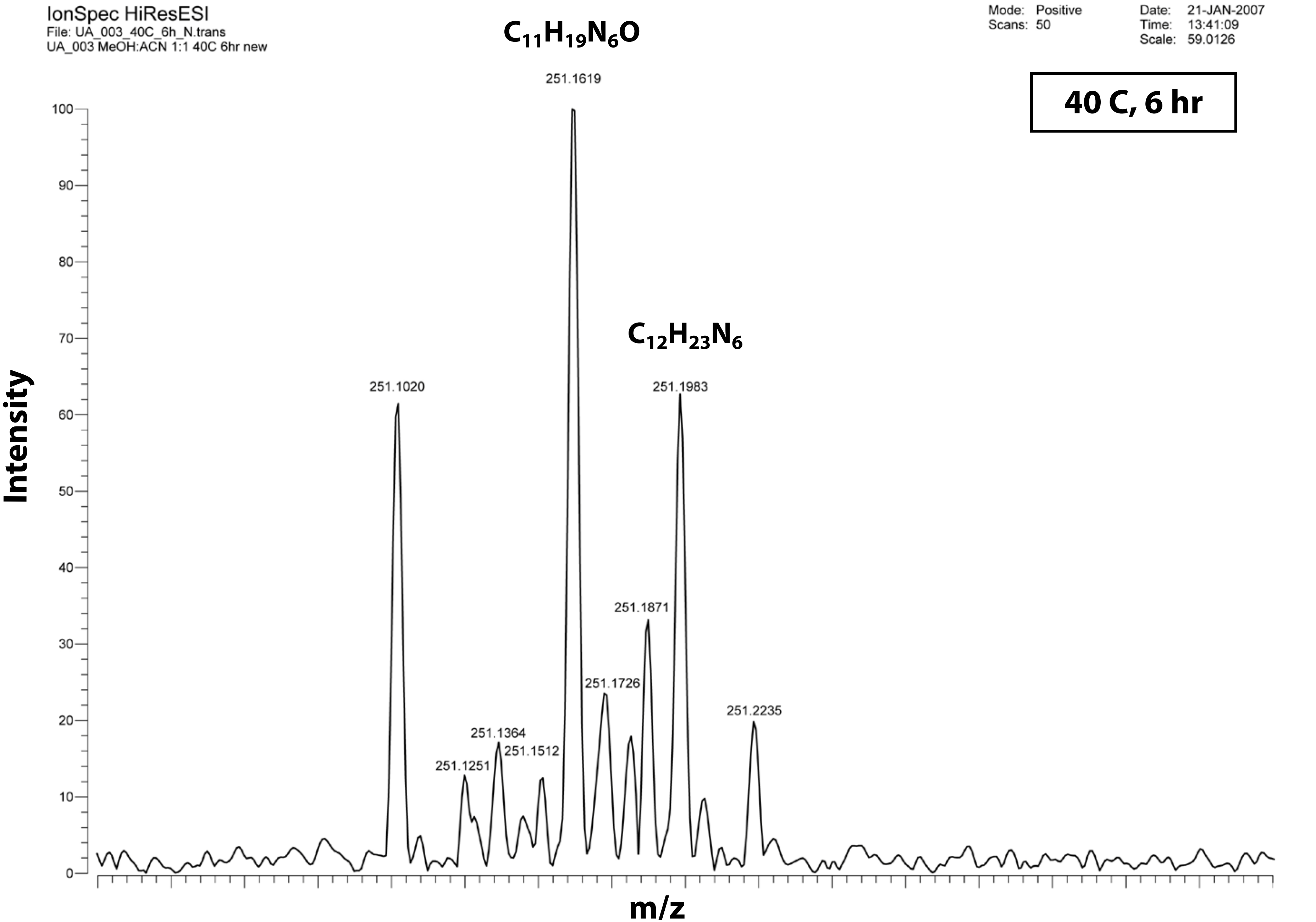


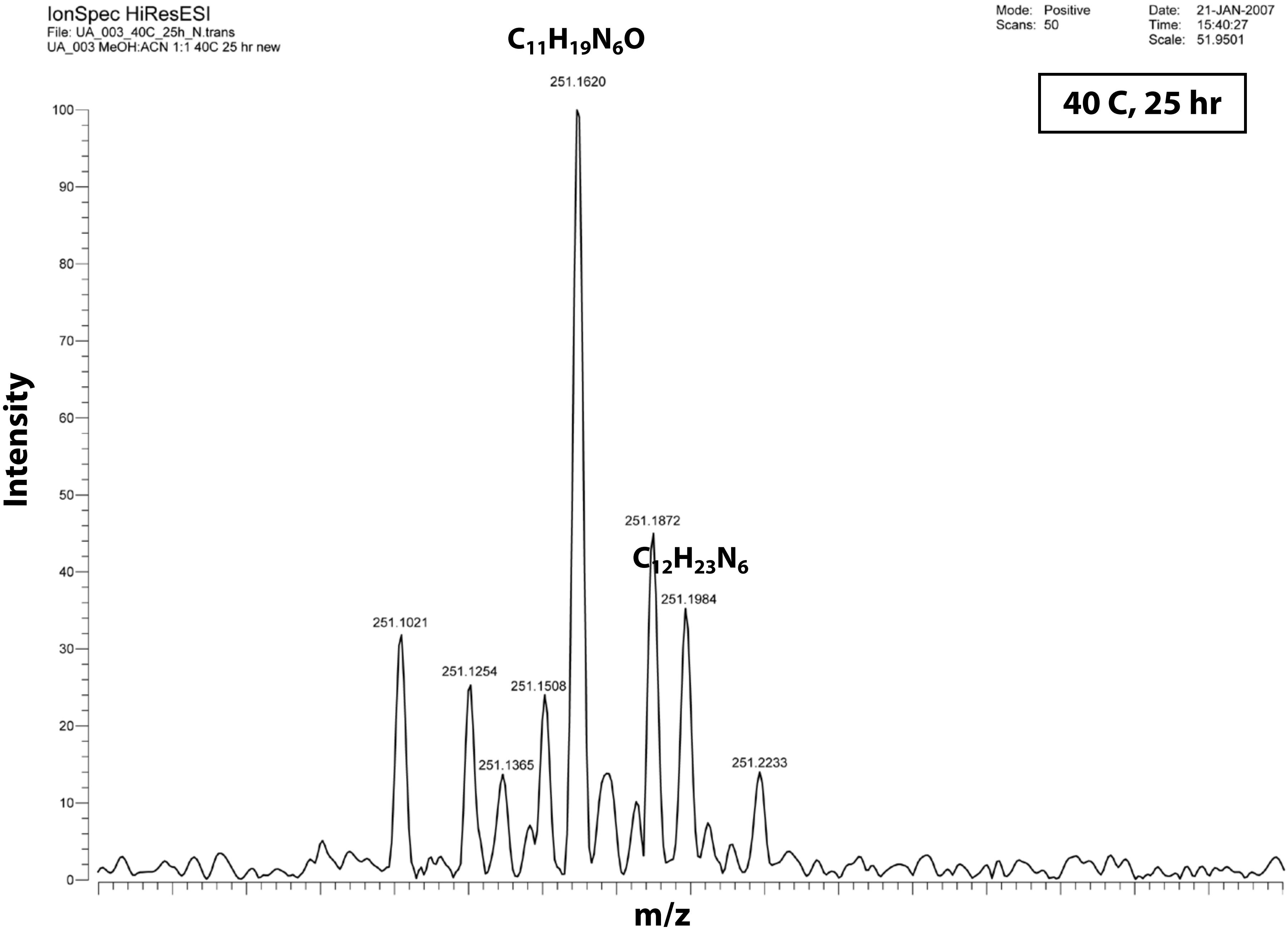
$C_{16}H_{36}N$
(internal standard)
$C_{12}H_{17}N_6$
$C_{12}H_{19}N_6$
$C_{11}H_{16}N_7$
Mode: Positive
Scans: 50
Date: 21-JAN-2007
Time: 13:41:09
Scale: 11.4952
40 C, 6 hr
242.2848
243.1351
243.2875
244.1559
245.1512
246.1463
247.1662
248.1624
249.0858
249.1819
250.1777
251.1020
251.1619
Intensity
m/z
100
90
80
70
60
50
40
30
20
10
0



$C_{16}H_{36}N$
(internal standard)
Mode: Positive
Scans: 50
Date: 21-JAN-2007
Time: 15:40:27
Scale: 11.3311
40 C, 25 hr
242.2848
$C_{12}H_{17}N_6$
245.1513
$C_{12}H_{19}N_6$
$C_{11}H_{16}N_7$
247.1663
246.1714
244.1560
248.1876
243.1351
249.1820
250.1664
251.1620
243.2875
251.1021
249.0855
Intensity
m/z
100
90
80
70
60
50
40
30
20
10
0

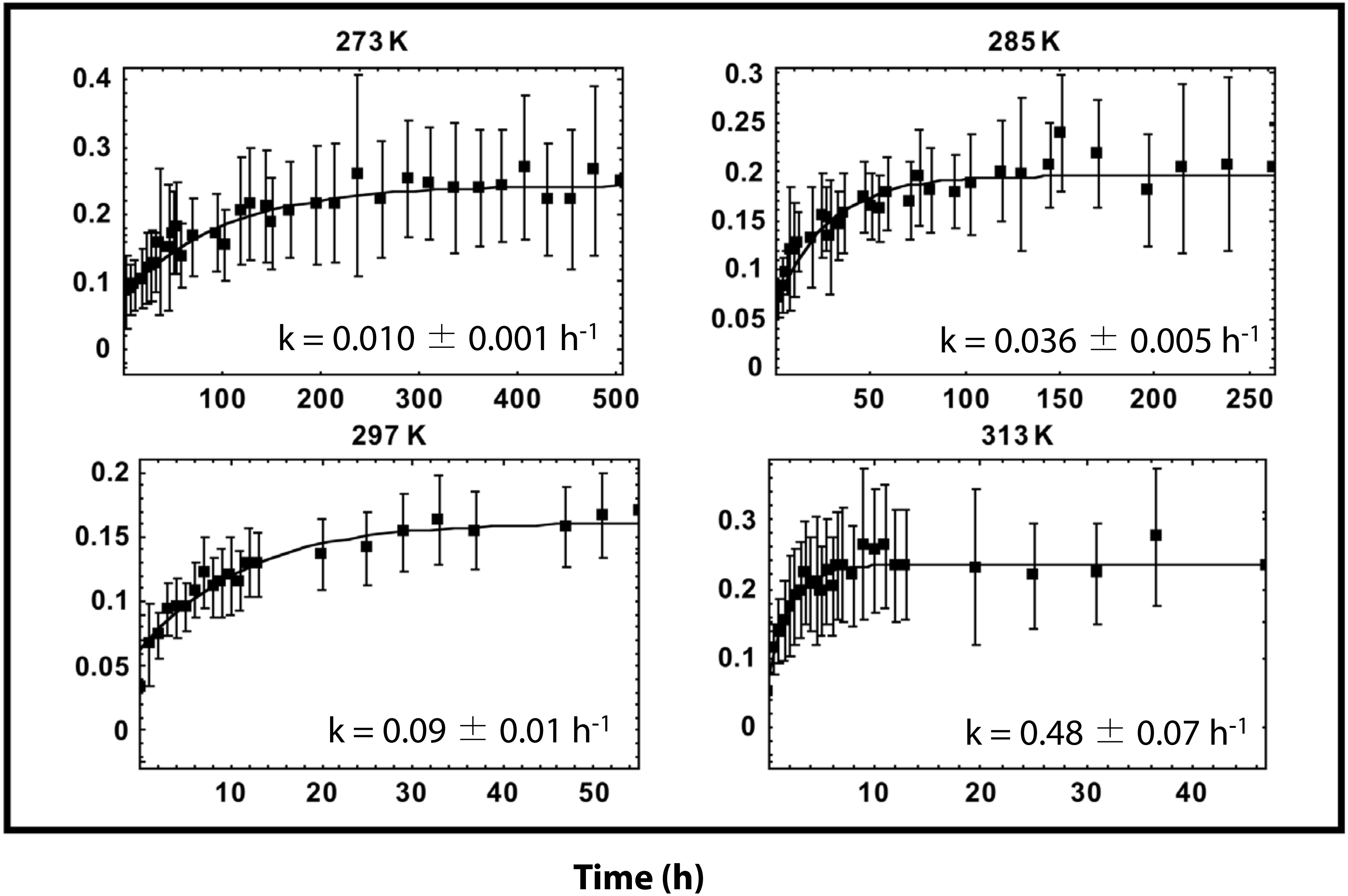

IonSpec HiResESI
File: UA_003_40C_0h_N.trans
UA_003 MeOH:ACN 1:1 40C 0hr new
Mode: Positive
Scans: 50
Date: 21-JAN-2007
Time: 10:57:14
Scale: 52.6242
40 C, 0 hr
$C_{12}H_{23}N_6$
$C_{11}H_{19}N_6O$
251.1984
251.1020
251.1731
251.1620
251.2237
251.1275
251.1360
Intensity
m/z
100
90
80
70
60
50
40
30
20
10
0


IonSpec HiResESI
File: UA_003_40C_6h_N.trans
UA_003 MeOH:ACN 1:1 40C 6hr new
Mode: Positive
Scans: 50
Date: 21-JAN-2007
Time: 13:41:09
Scale: 59.0126
40 C, 6 hr
C11H19N6O
C12H23N6
251.1619
251.1020
251.1983
251.1871
251.1726
251.2235
251.1364
251.1512
251.1251
Intensity
m/z
100
90
80
70
60
50
40
30
20
10
0


IonSpec HiResESI
File: UA_003_40C_25h_N.trans
UA_003 MeOH:ACN 1:1 40C 25 hr new
Mode: Positive
Scans: 50
Date: 21-JAN-2007
Time: 15:40:27
Scale: 51.9501
$C_{11}H_{19}N_6O$
251.1620
40 C, 25 hr
251.1872
$C_{12}H_{23}N_6$
251.1984
251.1021
251.1254
251.1508
251.1365
251.2233
Intensity
m/z
0
10
20
30
40
50
60
70
80
90
100

$[M+H]^+$: 251.162
($C_{11}H_{19}N_6O$)

$$[A]=[A]_0(1-e^{-k}\ )+^{t}c$$

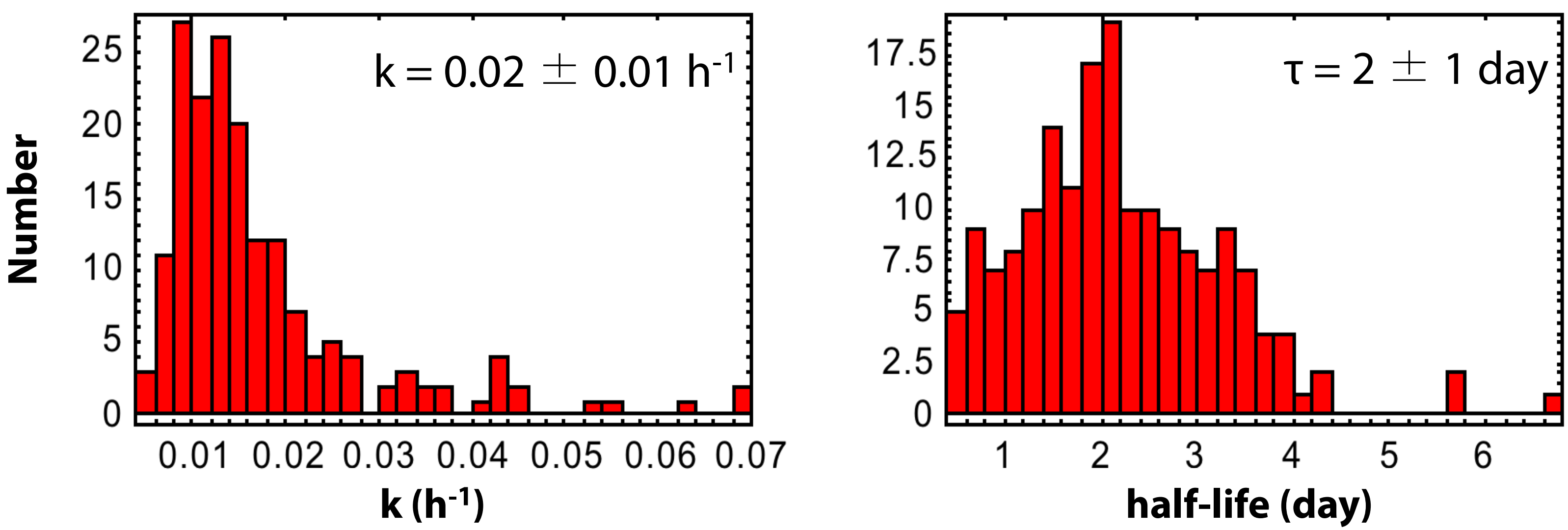


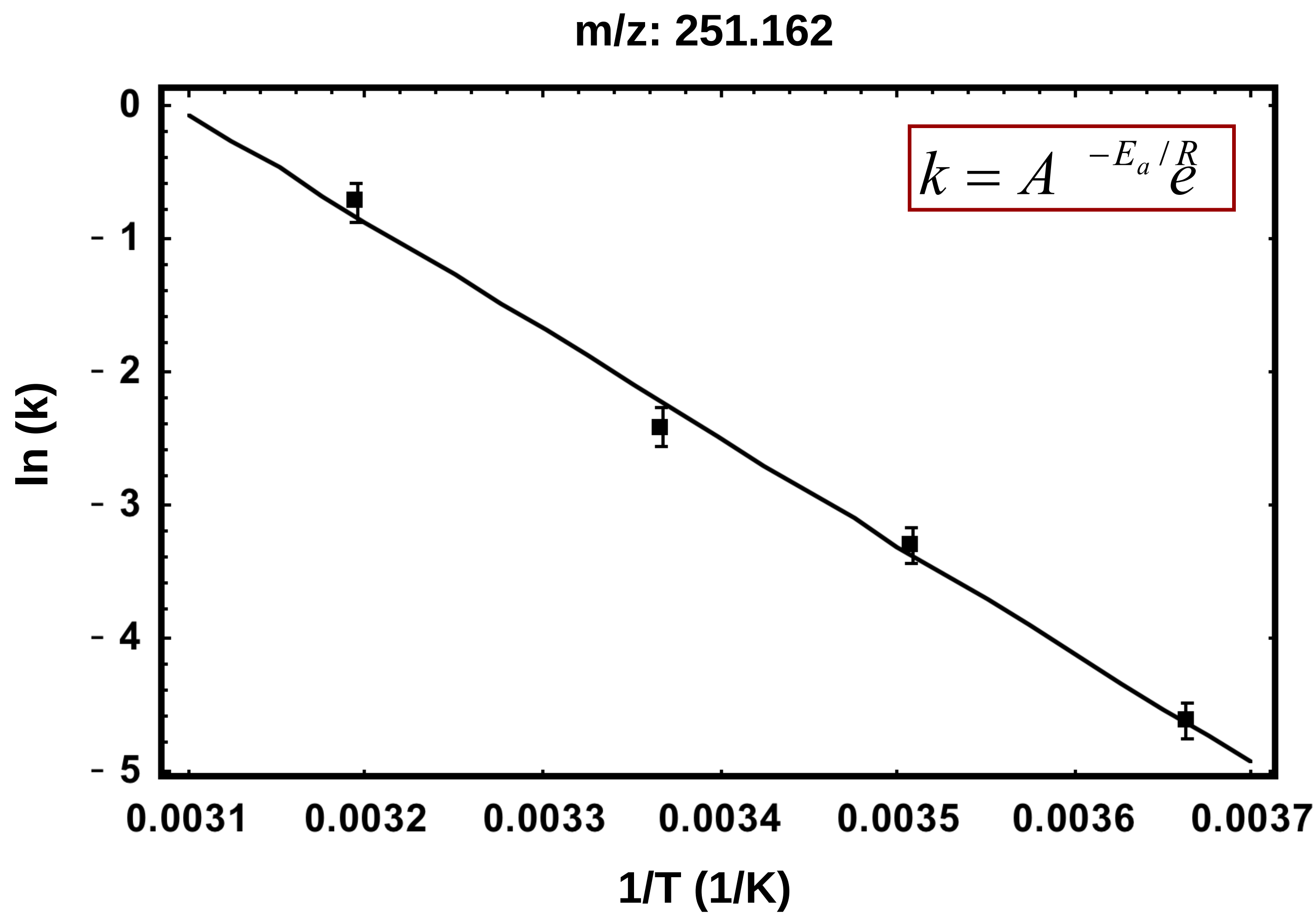
kinetics

Examine all reactions at 273 K:

• Observed growth curves had half-lives of **0.4 - 7 days**

This should provide enough time for interesting prebiotic reactions to take place in impact melts and cryolavas on Titan, as well as frozen ponds on the early Earth



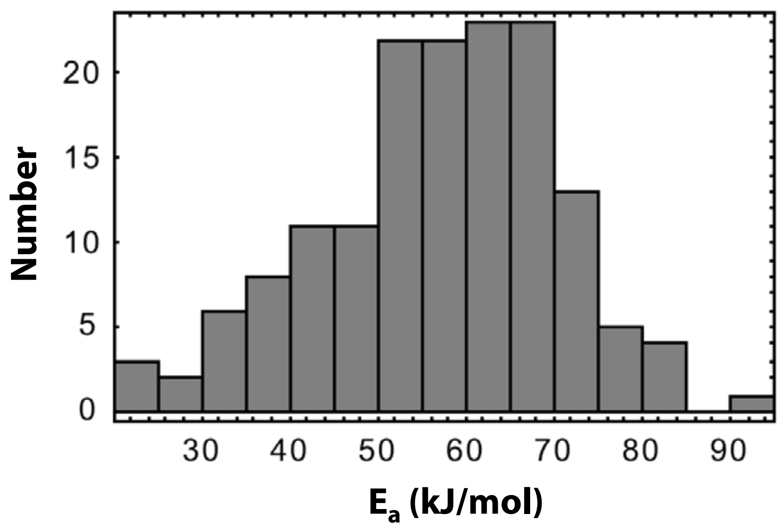

m/z: 251.162
$k = A e^{-E_a/R}$
0
- 1
- 2
- 3
- 4
- 5
ln (k)
0.0031
0.0032
0.0033
0.0034
0.0035
0.0036
0.0037
1/T (1/K)

E_a = 67 +/- 4 kJ/mol

activation energies

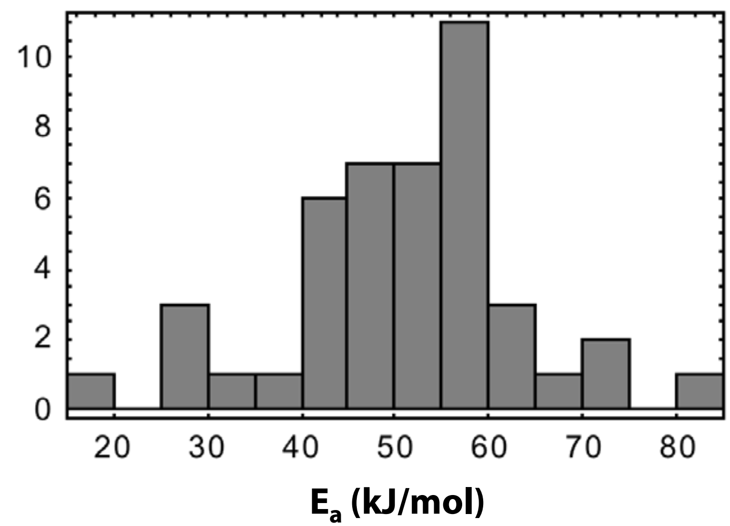
We repeated the same calculation for all oxygenated species there grew over time, and all non-oxygenated species that decayed over time

Growth Curves



$\langle E_a \rangle \sim 60$ +/- 10 kJ/mol

Decay Curves



$\langle E_a \rangle = 50$ +/- 10 kJ/mol

The activation enthalpies for **aliphatic imines** at neutral pH are found in the range of **50–60 kJ/mol** kinetics

If similar reactions took place in concentrated ammonia solutions at 176 K, how long would they take?

$$k = A^{-E_a/RT}$$

Take… $E_a = 60$ kJ/mol

$T_1 = 273$ K $T_2 = 176$ K

$k_1 = (1\text{ day})^{-1}$ $R = 8.3$ J/K/mol

These reactions would take **~6000 years at 176 K**.

Question #3:

Nature of tholin hydrolysis products

From Neish et al. (2010)

Hang on…

- Were any biomolecules formed in these experiments?

Previous work:

- Khare et al. (1986) and Raulin et al. (2007) hydrolyzed Titan haze analogues at *high temperature* (70 - 100° C) for *short timescales* (24 – 48 h)
- Produced amino acids glycine, alanine, and aspartic acid, as well as urea

Present work:

- Hydrolyze Titan haze analogues at *low temperature* (253-293 K) over *long timescales* (~1 year)

molecular structure

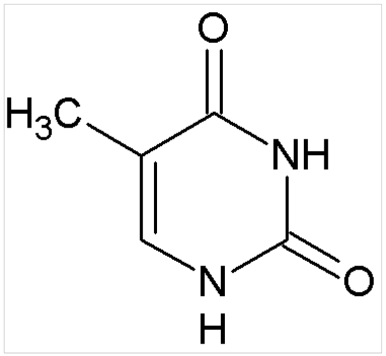
- We searched through the species observable with our instrument (m/z ~110-400), and found masses consistent with almost all **amino acids** and **nucleobases**, at varying intensities

- **Wait!** Mass alone is not enough to determine whether biomolecules are present in our sample
  - Such large, complicated molecules can take one of many different structures

- To determine structure, we **fragmented** the molecules by quadrapole collision-induced dissociation (QCID) and infrared multiphoton dissociation (IRMPD), and compared them to fragmentation spectra of pure biomolecules molecular structure

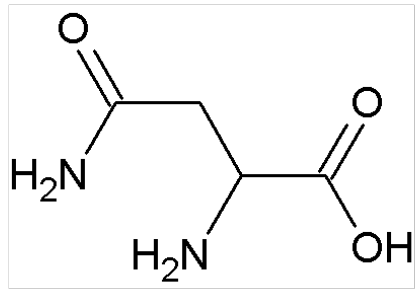
We focused on six molecules of strong intensity:

nucleobase

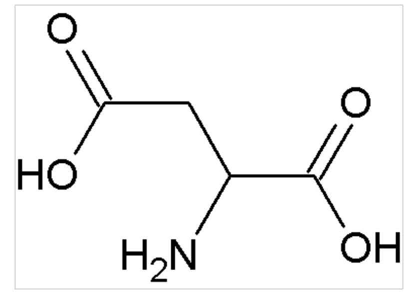


Thymine

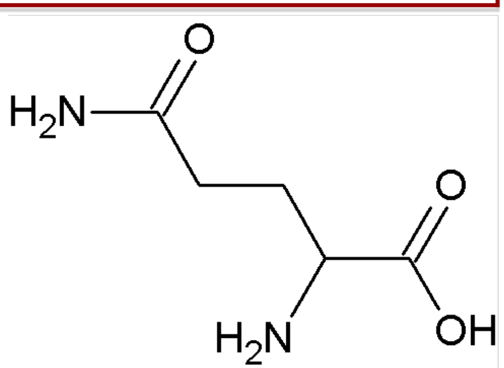
amino acids



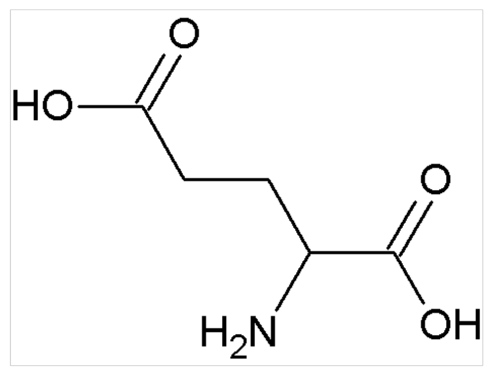
Asparagine



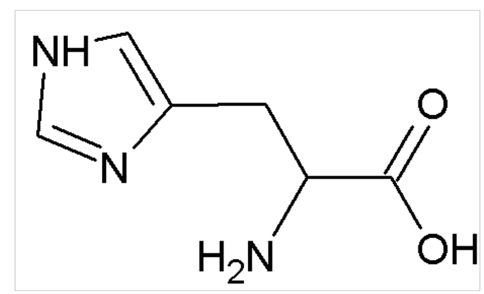
Aspartic Acid



Glutamine



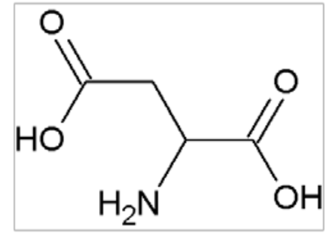
Glutamic Acid



Histidine

positive example

Aspartic Acid ($C_4H_6NO_4^-$)



Aspartic Acid (IRMPD)

* = noise

-CO$_2$

-COOHNH$_2$

-H$_2$O

$C_4H_6NO_4^-$

-COOHOH

-H$_2$O$_2$

-NH$_3$

Intensity

Hydrolyzed Tholin (293 K, 1 year)

-H$_2$O

$C_4H_6NO_4^-$

-CO$_2$

-COOHNH$_2$

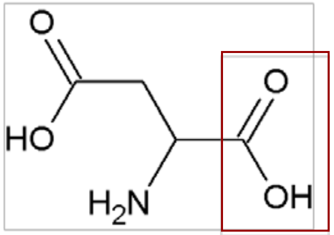
-H$_2$O$_2$

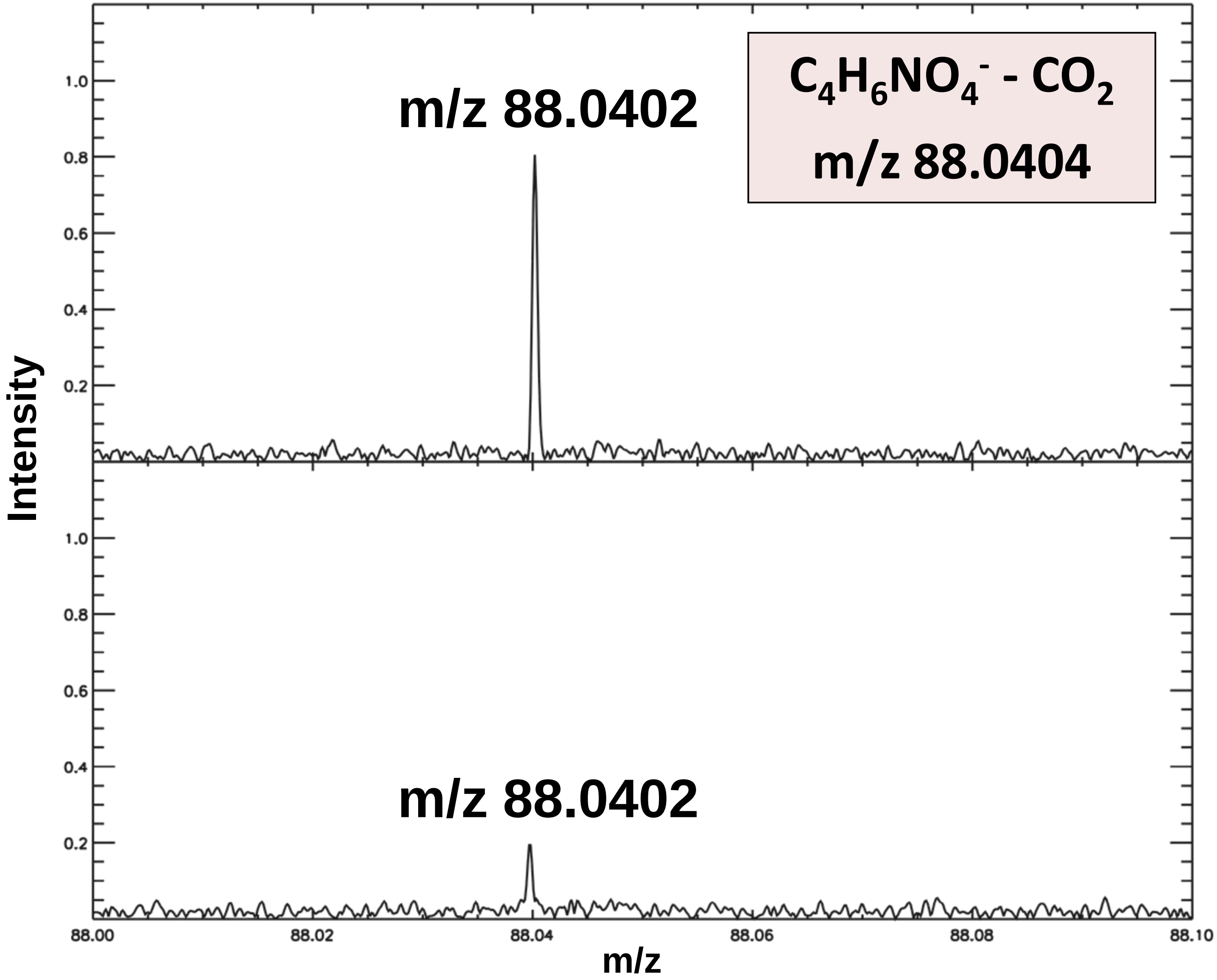
-NH$_3$

m/z

positive example

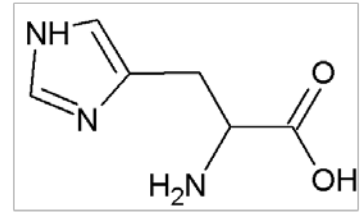
Aspartic Acid ($C_4H_6NO_4^-$)





negative example

Histidine ($C_6H_8N_3O_2^-$)



Histidine (IRMPD)

* = noise

$C_6H_8N_3O_2^-$

$-C_2H_3NO_2$

$-COOHNH_2$

$-CH_3NO$

$-2H_2O$

$-H_2O$

$-NH_3$

Intensity

Hydrolyzed Tholin (253 K, 1 year)

$C_6H_8N_3O_2^-$

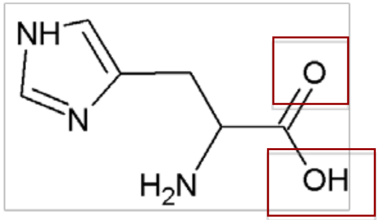
$-H_2O$

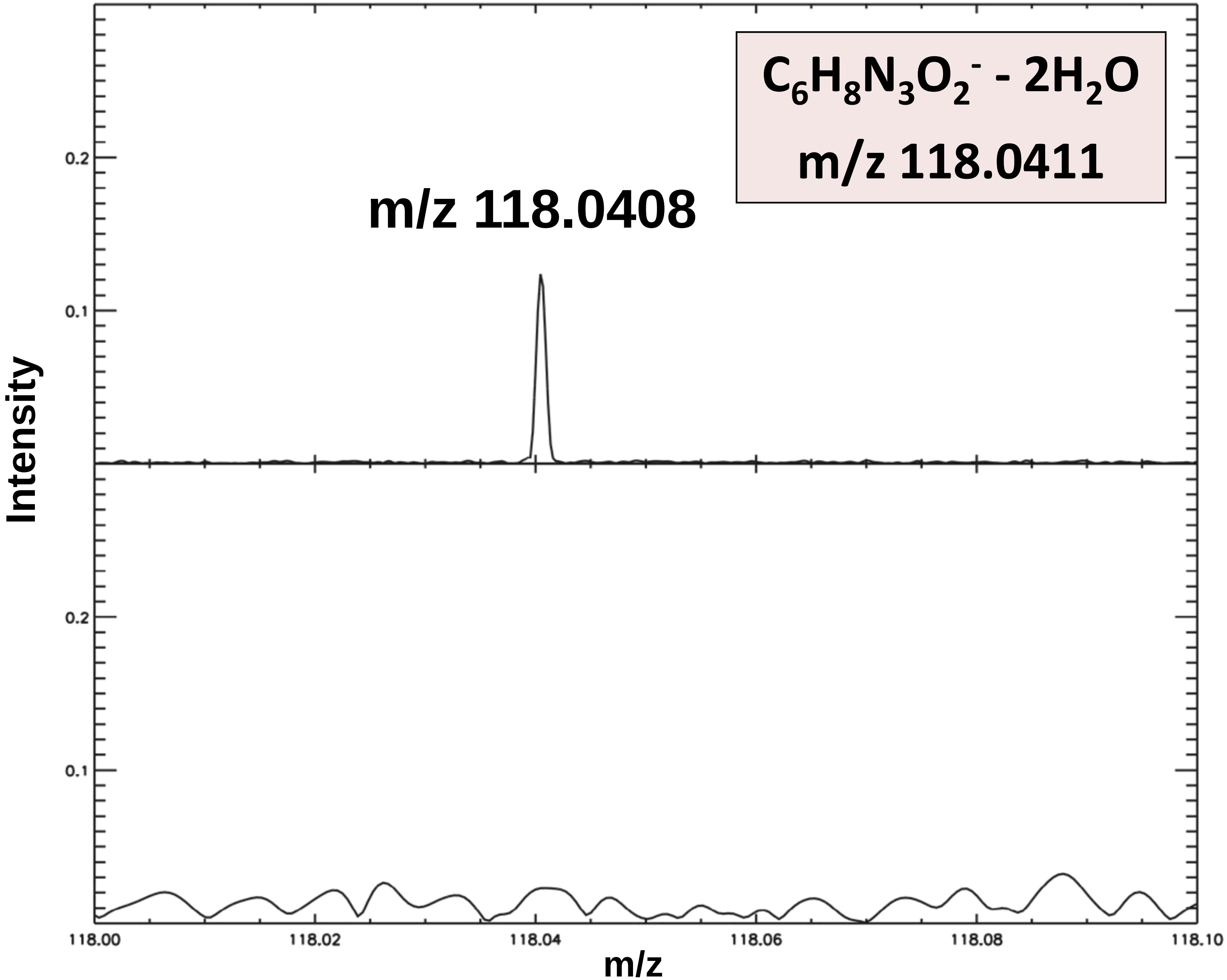
$-C_2H_4N_2$

m/z

negative example

Histidine ($C_6H_8N_3O_2^-$)

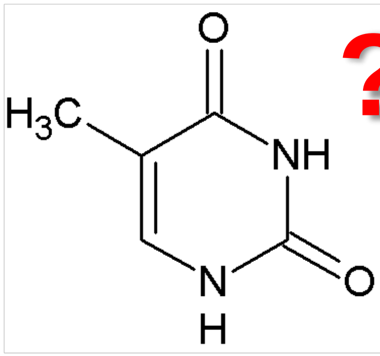




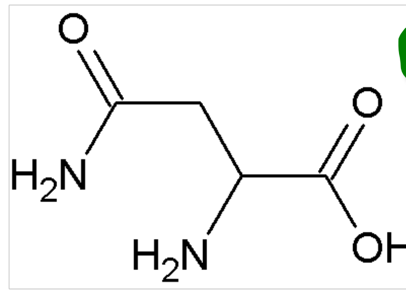
We focused on six molecules of strong intensity:

nucleobase

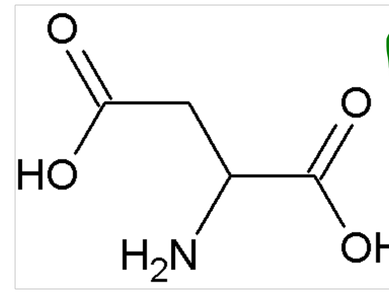
amino acids



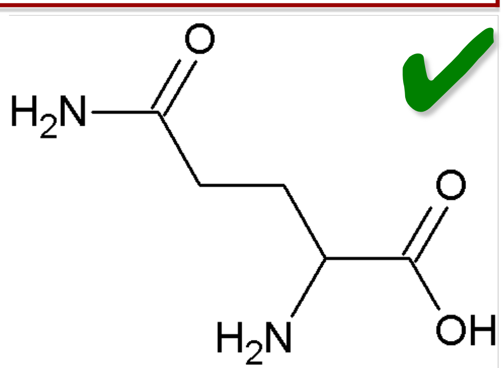
Thymine



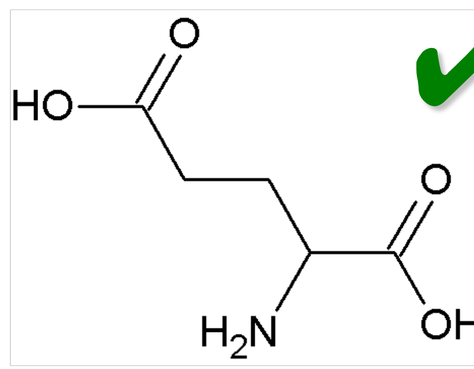
Asparagine



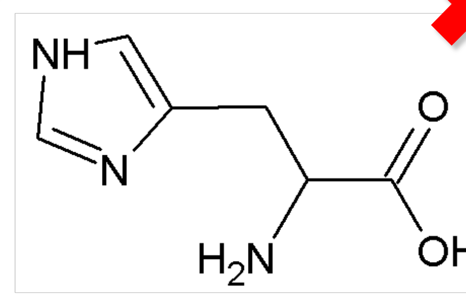
Aspartic Acid



Glutamine



Glutamic Acid



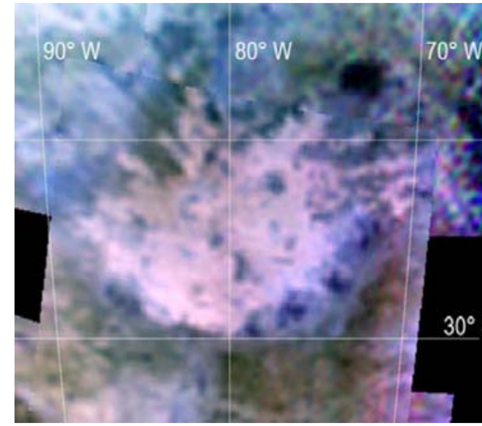
Histidine

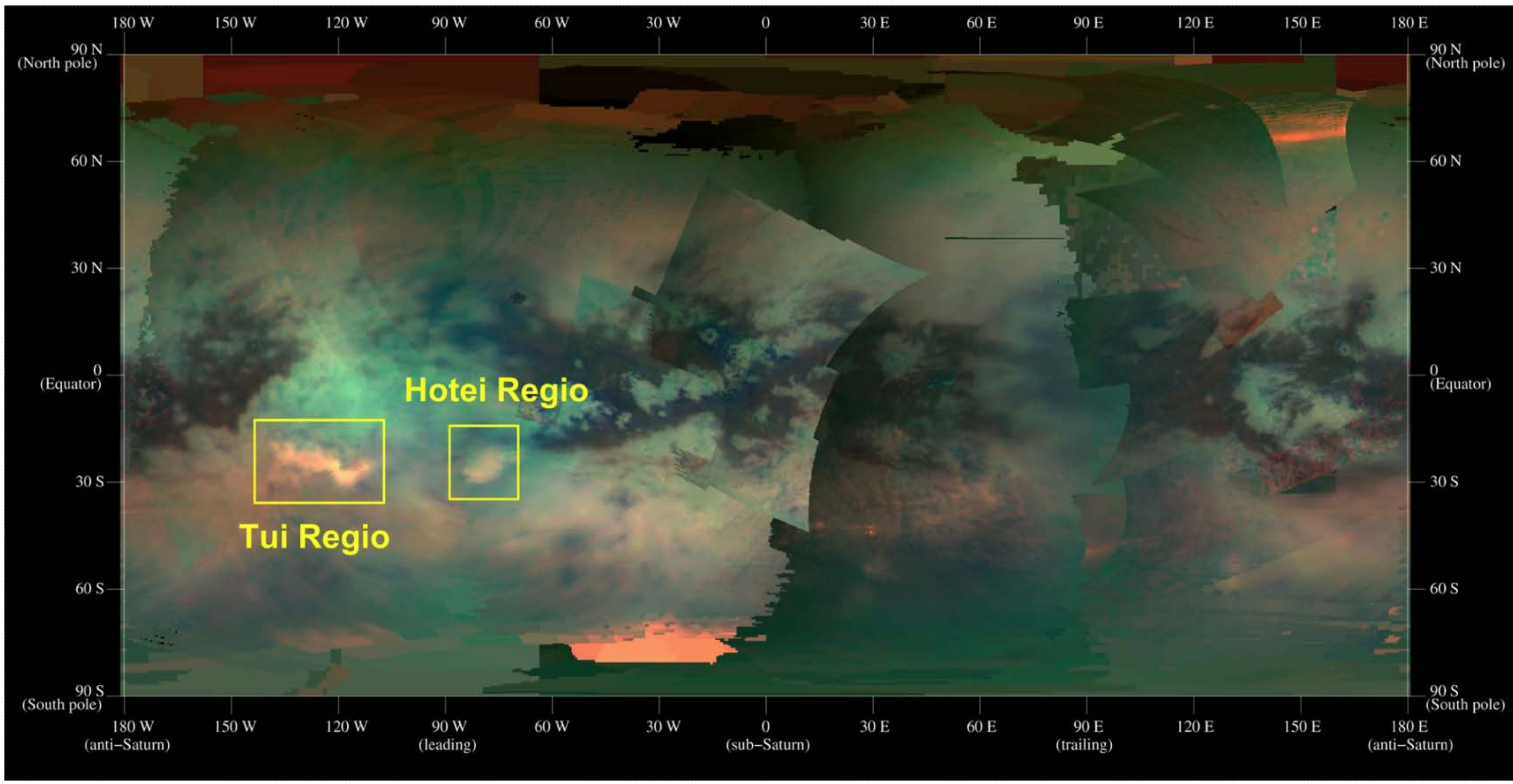
Extra credit:

Detection of biomolecules on Titan

hotei and tui regio

Hotei and Tui Regio are unusually bright at 5 μm. Their lobate, flow-like morphology suggests a cryovolcanic origin.

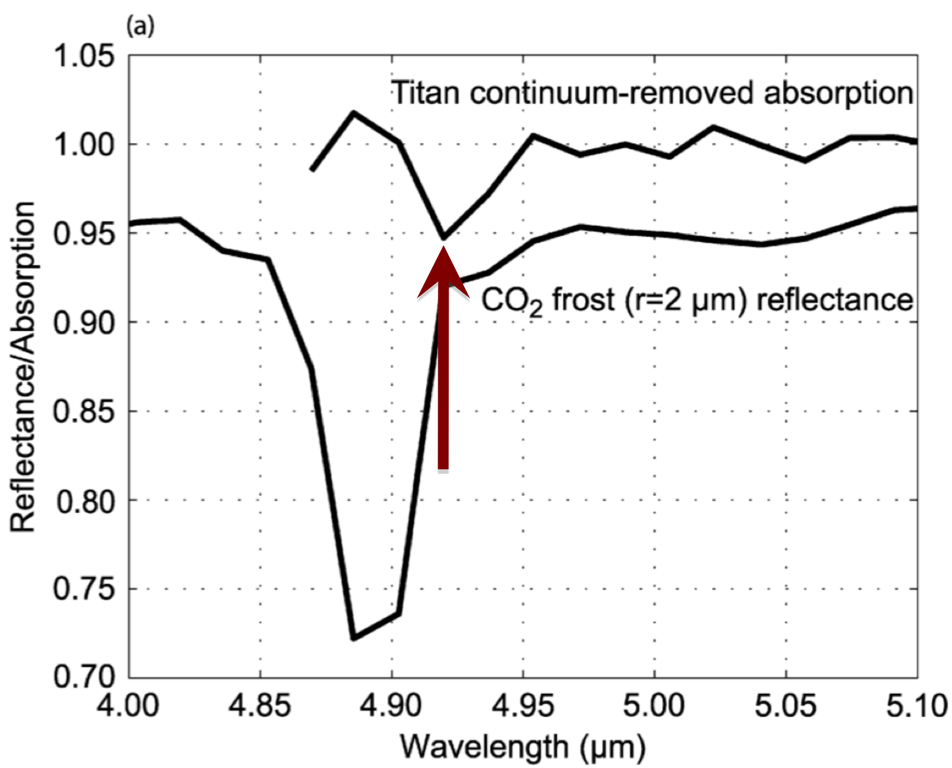




Barnes et al. 2005, Barnes et al. 2006, Soderblom et al. 2009

spectroscopy

A spectral feature at 4.92
μm has been discovered
in Tui Regio. This is the only absorption feature that has yet been detected on Titan's surface, and there has been as yet no adequate identification of this feature.



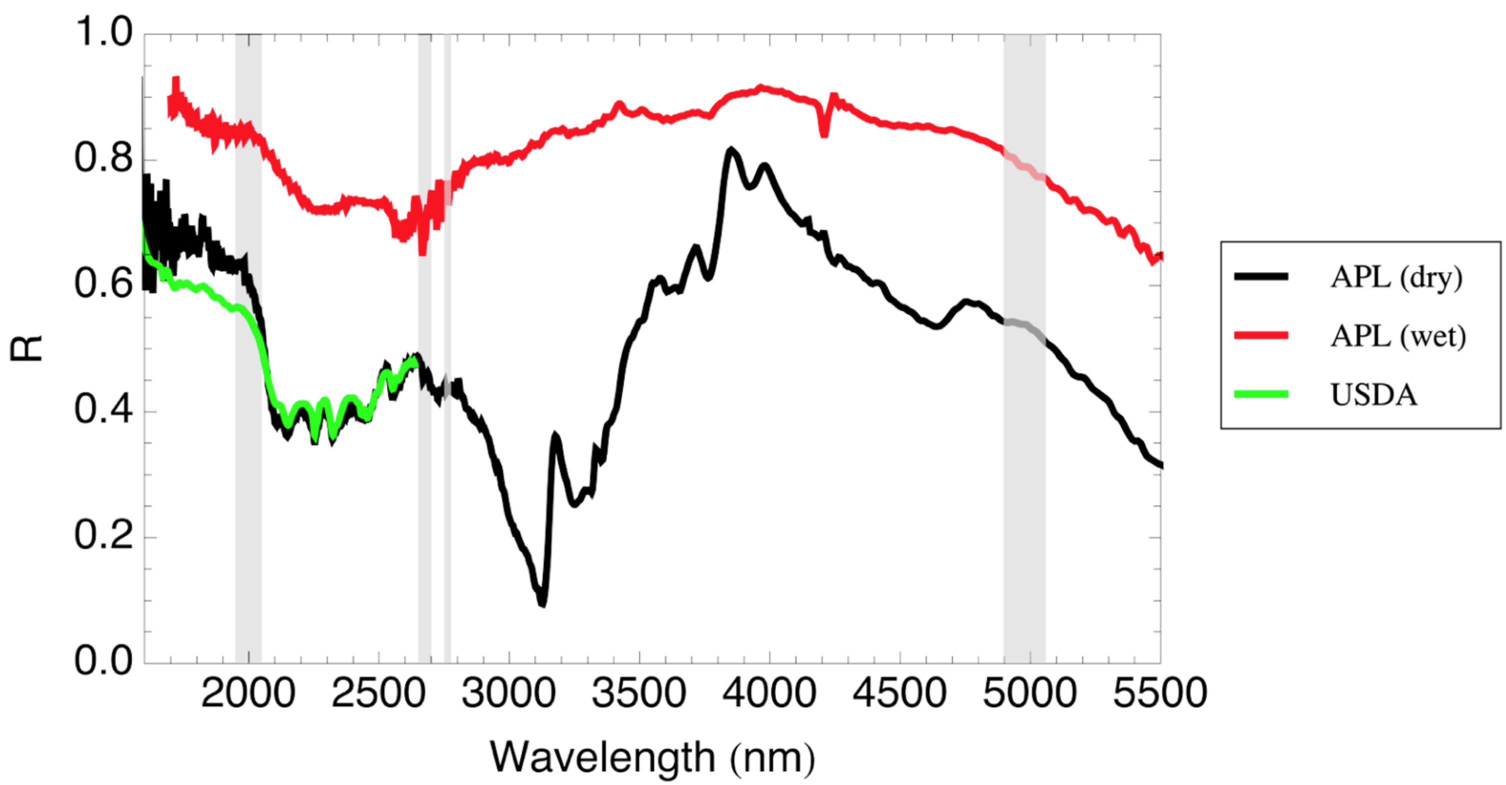
Could this feature be caused by the presence of biomolecules?

McCord et al. 2008

spectroscopy

We propose to acquire spectra of biomolecules in this wavelength range, and compare them to VIMS data from Tui and Hotei Regio.

Initial results for **glycine**:



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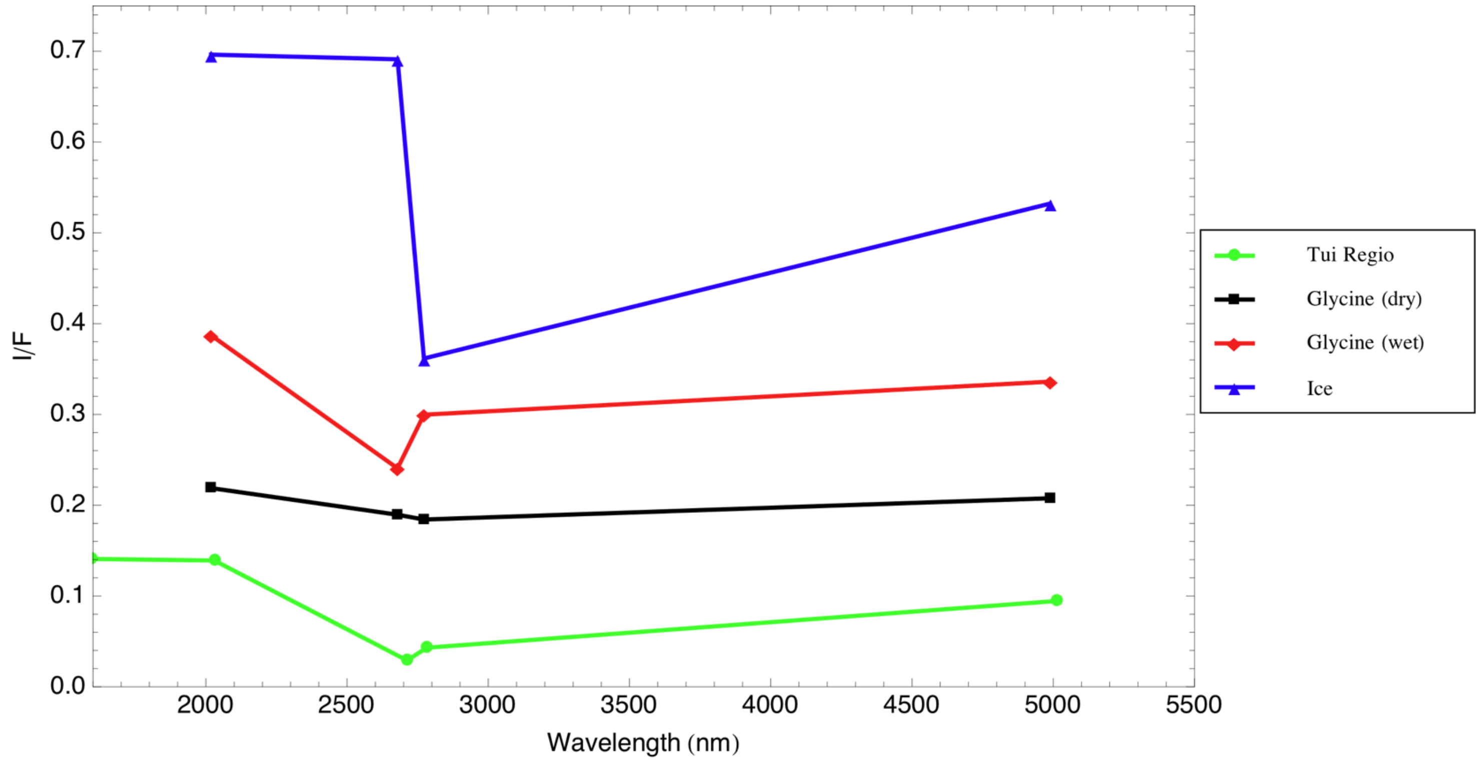

conclusions

When Titan haze analogues are placed in liquid water, they produce oxygenated species via hydrolysis reactions with activation energies of ~ 60 ± 10 kJ mol^{-1}

Oxygen incorporation is ***very fast*** compared to planetary timescales for which liquid water can exist

Four amino acids were identified in a tholin sample that had been hydrolyzed in 13 wt. % ammonia-water at 253 K and 293 K for a year

- This represents the first detection of biomolecules created under conditions similar to those found in transient liquid environments on Titan

Future mission targets:

1. Impact craters
2. Cryovolcanic flows

Why?

Oxygenated species, possibly prebiotic in nature, will be present at these locales

Image by Tibor Balint