Isotopic ratios in HCN and HC_3N in Titan's atmosphere derived from Cassini/CIRS observations

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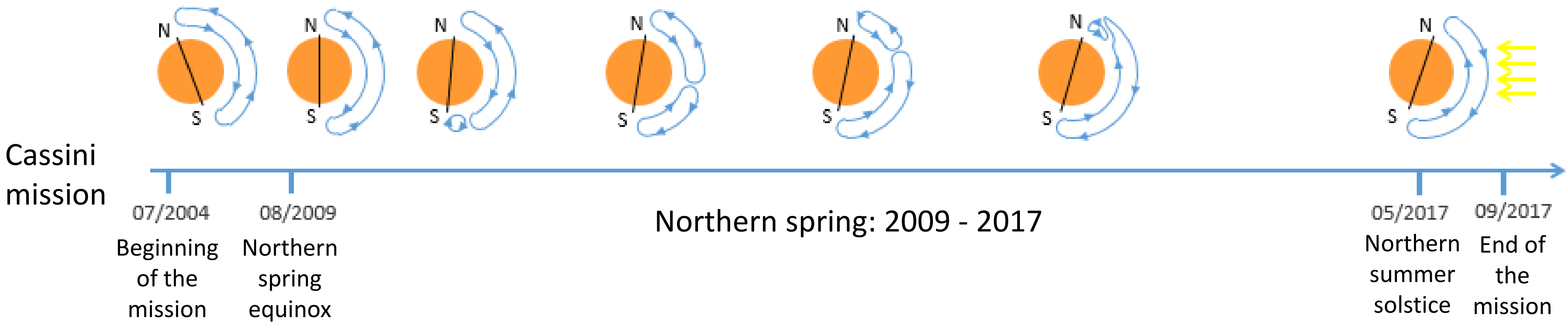
Introduction

Wealth of molecules are formed from the dissociation of N_2 and CH_4 by photons and magnetospheric e- in the upper atmosphere of Titan.

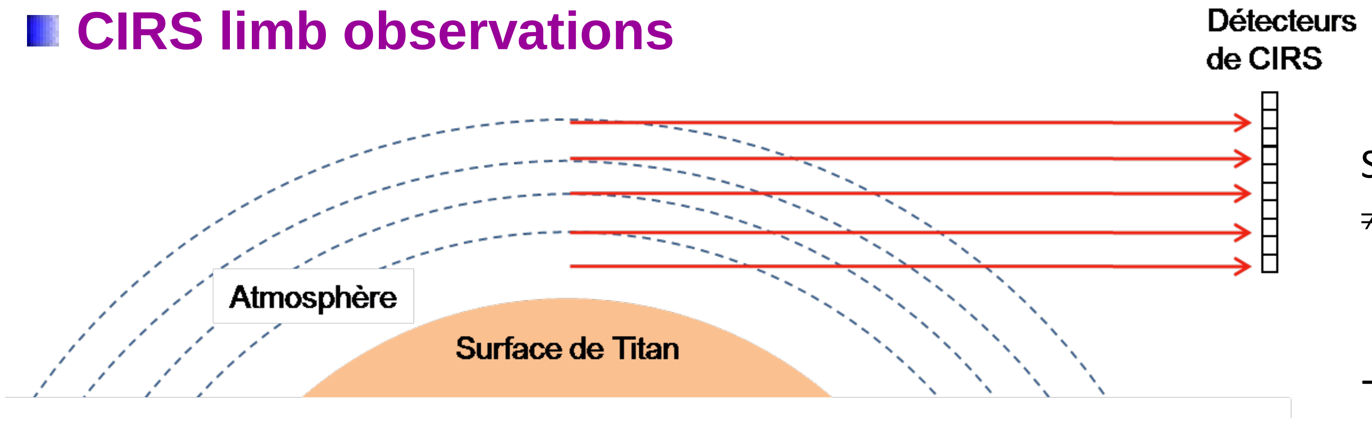
Isotopic ratios in the produced photochemical species probe atmospheric chemical or photochemical fractionation processes, which can enrich or deplete isotopologues.

Goal: we derive the **$^{14}N/^{15}N$ and $^{12}C/^{13}C$ isotopic ratios in HCN and HC_3N using all Cassini/CIRS data.**
-> **derive precise isotopic ratio values.**
-> infer **potential spatially or seasonally variations** following seasonal changes of the global dynamics?



Cassini/CIRS observations

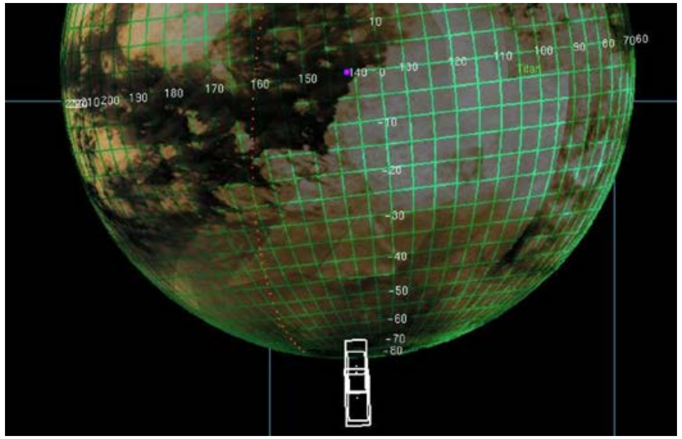
CIRS limb observations

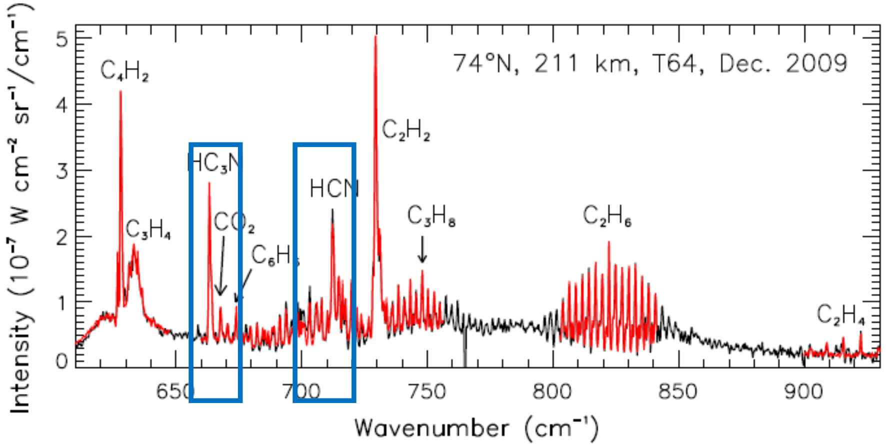


Spectra acquired at ≠ altitudes → Vertical profiles of temperature and molecular abundances

- Probed altitudes: 120 - 650 km
- Vertical resolution of ~30 km

Integrating mode: résolution spectrale = **0.5 cm^{-1}**





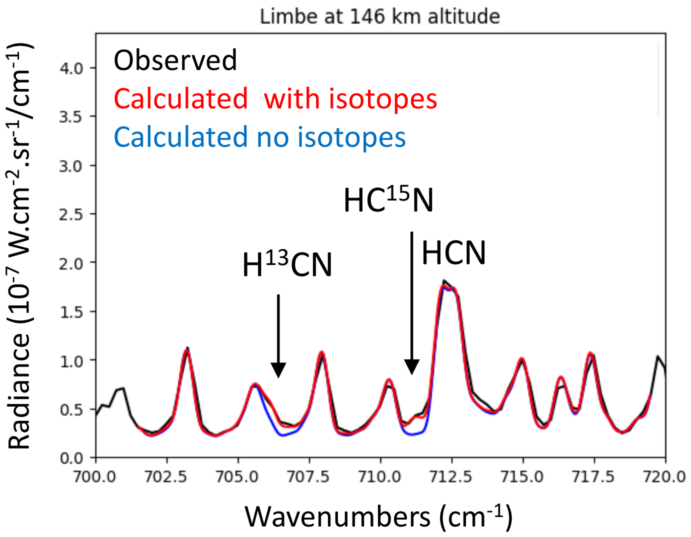
We use the entire CIRS limb dataset acquired at 0.5 cm^{-1} resolution from 2005 to 2017.

Method

We use an inversion algorithm and radiative transfer code to derive the HCN and HC_3N isotopologues abundances.

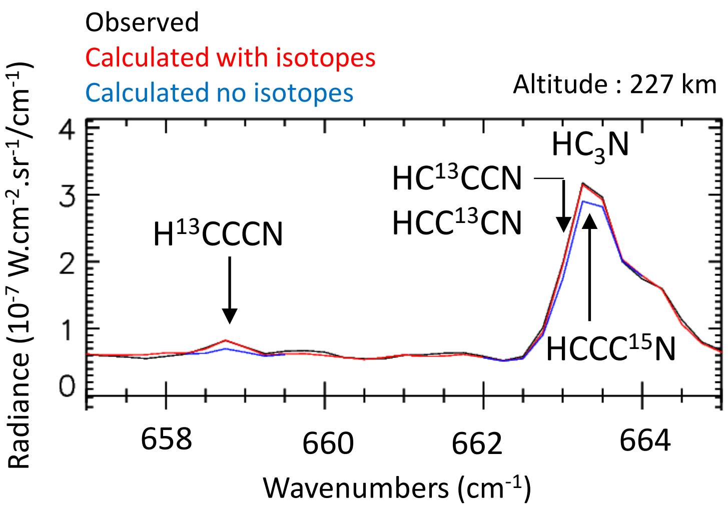
HCN isotopologues:

- $H^{13}CN$ at 706 cm^{-1}
- $HC^{15}N$ at 711 cm^{-1}



HC_3N isotopologues:

- $H^{13}CCCN$ at 658.7 cm^{-1}
- $HC^{13}CCN$ at 663.0 cm^{-1}
- $HCC^{13}CN$ at 663.0 cm^{-1}
- $HC_3{}^{15}N$ at 663.3 cm^{-1}



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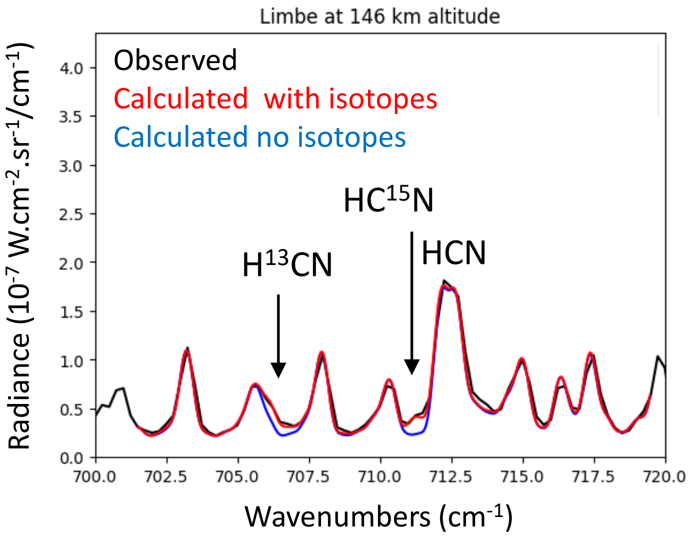

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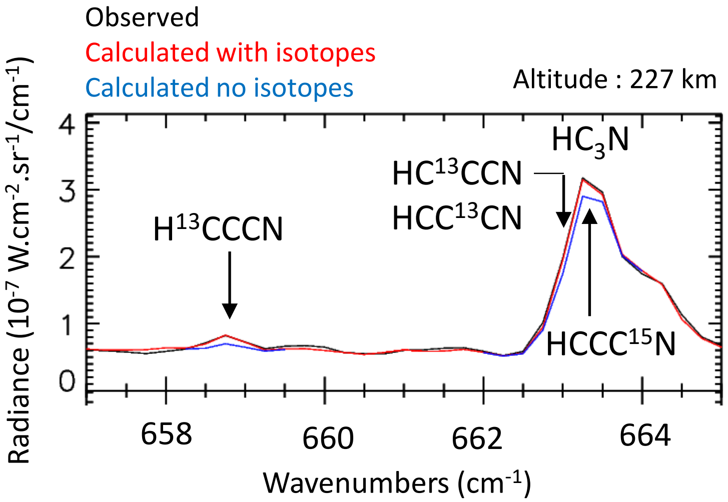
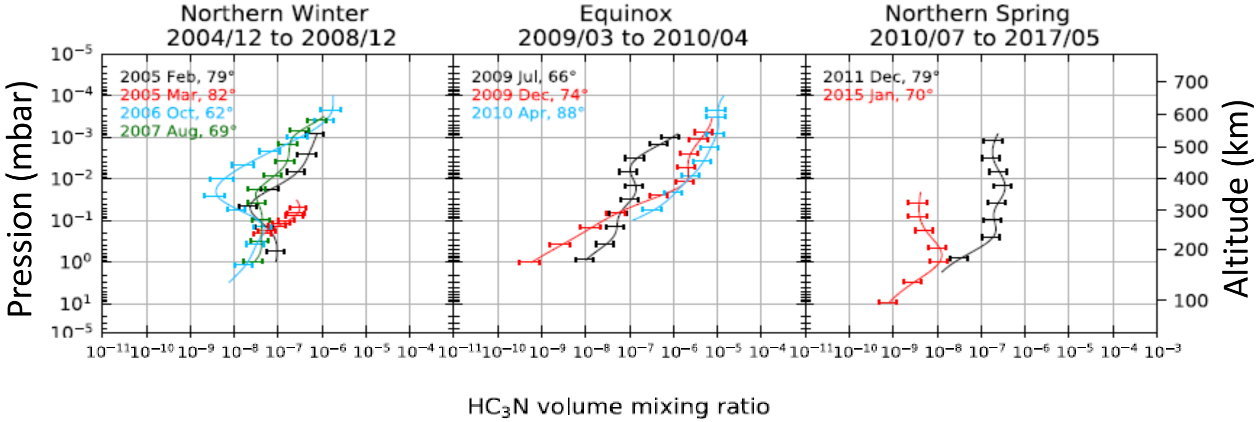
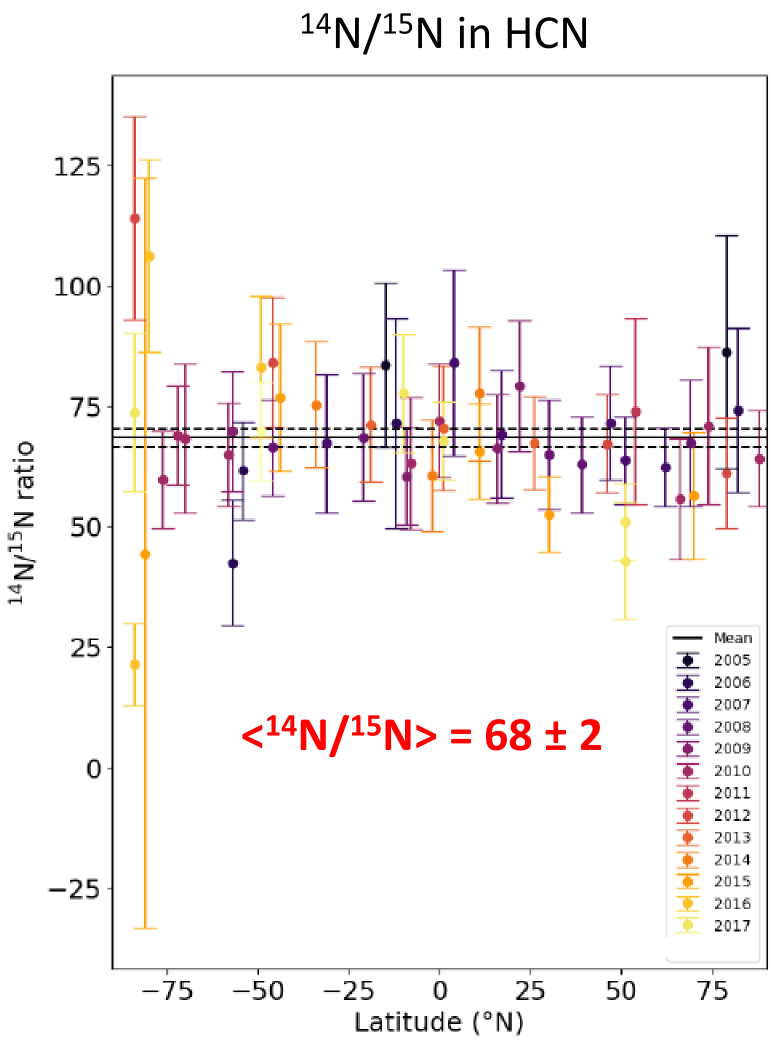


- we assume **no vertical variation of the isotopic ratios in the 200-500 km altitude range.**
- we use the thermal profiles and the HCN, HC_3N, CO_2, C_2H_2, CH_3C_2H, C_4H_2, C_6H_6 volume mixing ratios profiles from Mathé et al. (2020).
- **53 latitudes studied for HCN.**
- **13 polar latitudes studied for HC_3N.**



Mathé et al. (2020)

$^{14}N/^{15}N$ in HCN: results from CIRS data between 2005 and 2017



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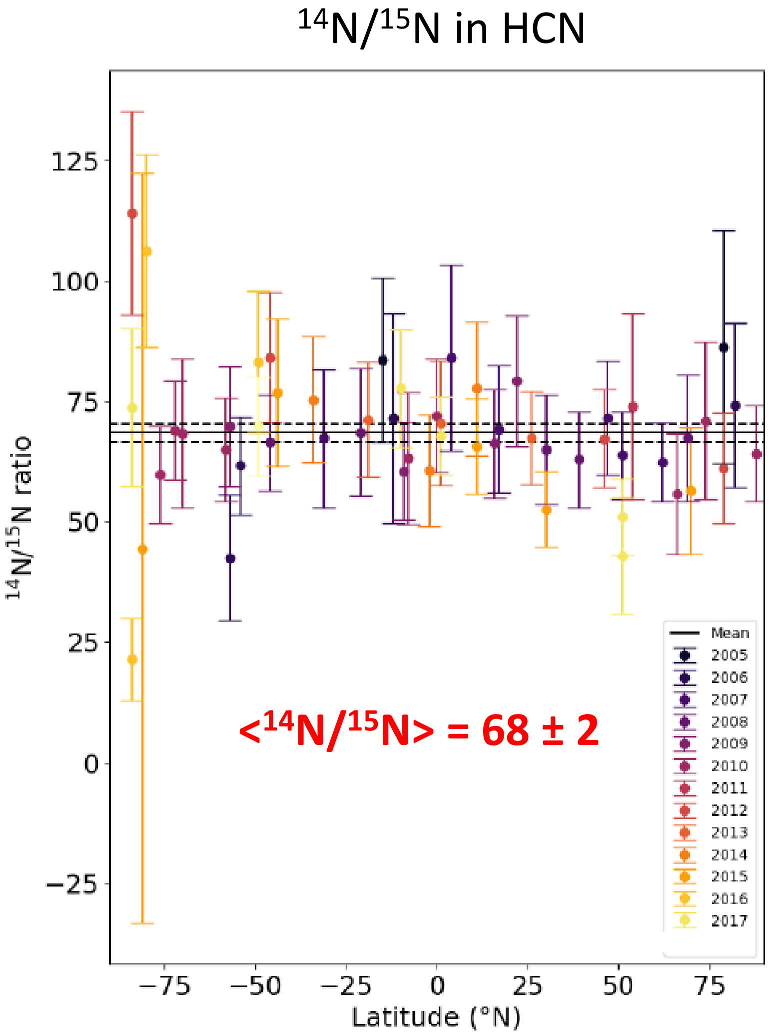


$^{14}N/^{15}N$ in HCN previous measurements

- Disk-averaged

65 ± 6.5	IRAM	*Marten et al. (2002)*
72 ± 9	SMA	*Gurwell et al. (2004) A*
94 ± 13	SMA	*Gurwell et al. (2004) B*
65 ± 12	SMA	*Gurwell et al. (2011)*
76 ± 6	Herschel/SPIRE	*Courtin et al. (2011)*
72.2 ± 2.2	ALMA	*Molter et al. (2016)*

- Spatially resolved

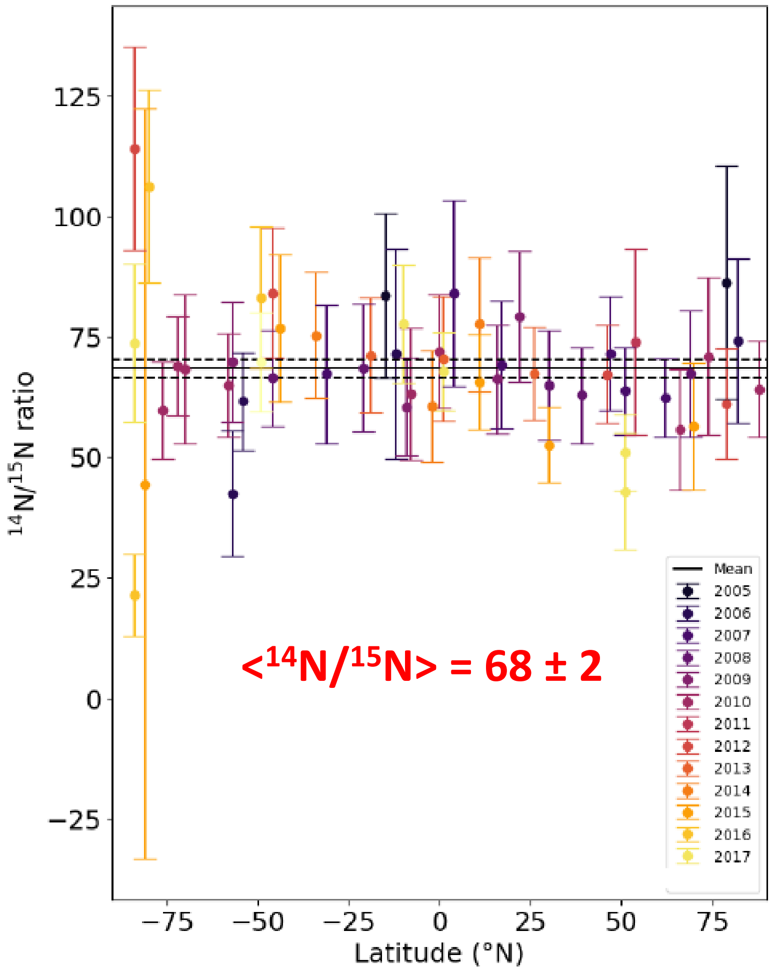
56 ± 8	Cassini/CIRS 15°S & 80°N in 2005	*Vinatier et al. (2007)*

$^{14}N/^{15}N$ dans N_2 = 167.6 ± 0.6 In situ measurements by Huygens/GCMS, *Niemann et al. (2010)*

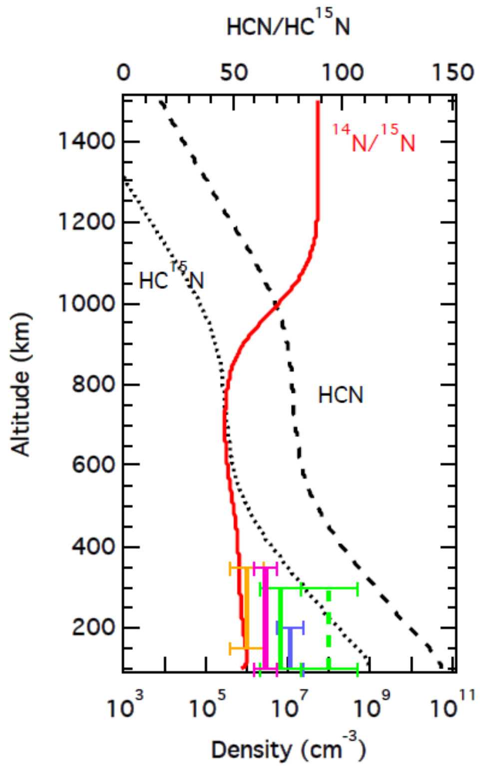
HCN is enriched in ^{15}N by a factor ~2.5 compared to N_2.

$^{14}N/^{15}N$ in HCN: results from CIRS data between 2005 and 2017

$^{14}N/^{15}N$ in HCN



Photochemical model of *Vuitton et al. (2019)*
-> $^{14}N/^{15}N$ in HCN increases with altitude



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fractionation process in the $^{14}N^{14}N$ and $^{14}N^{15}N$ photodissociation
=> formation of $HC^{15}N$ mostly below 800 km.

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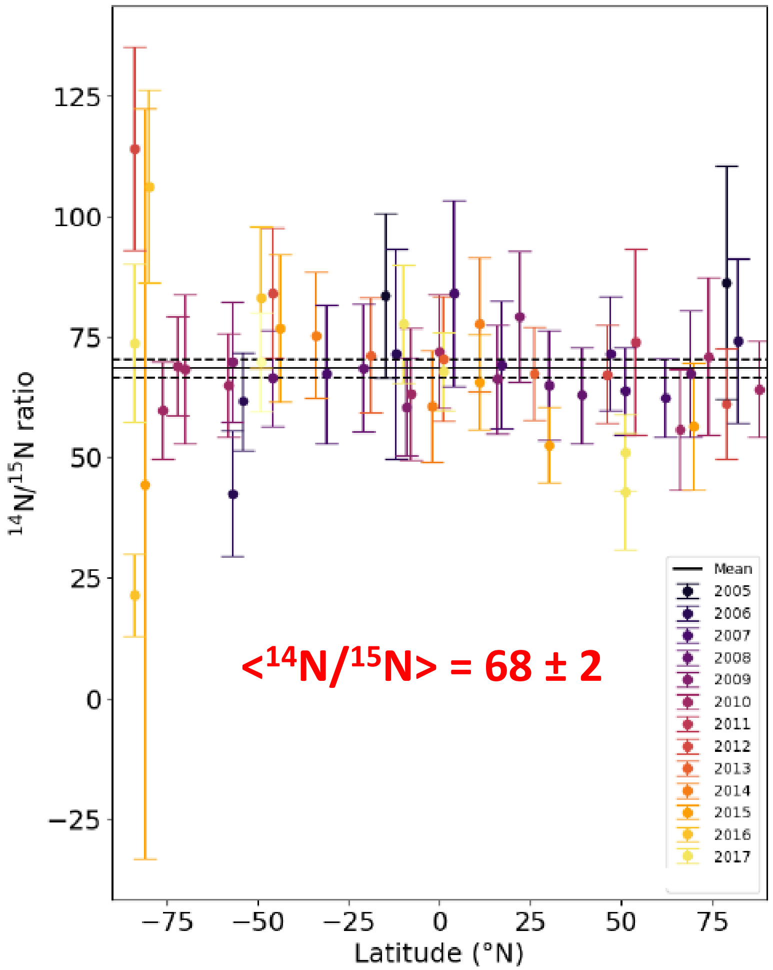

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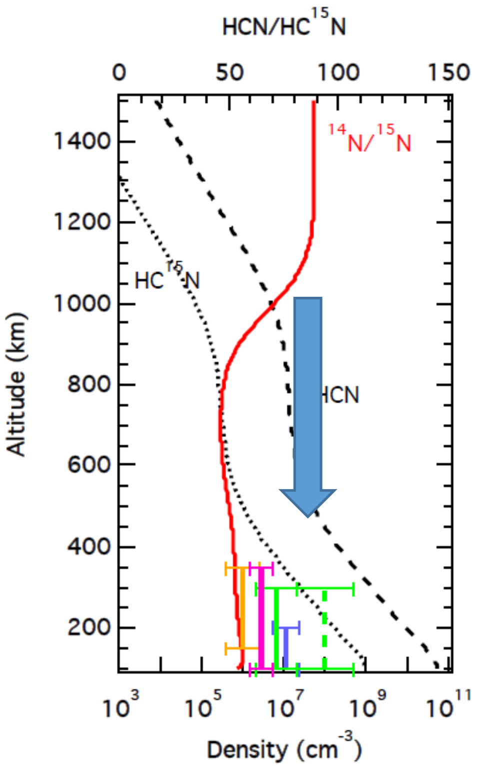

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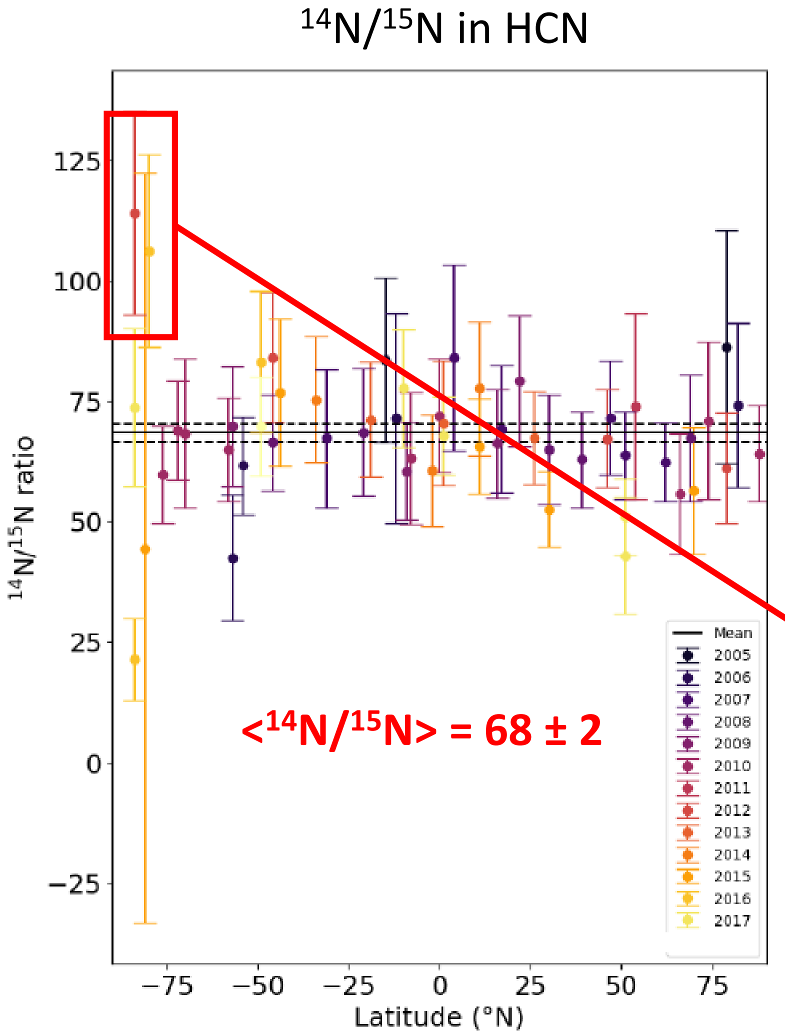
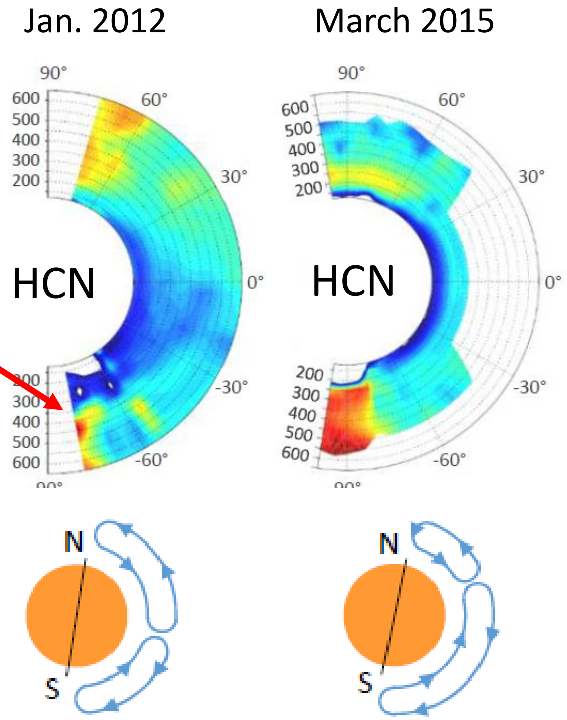
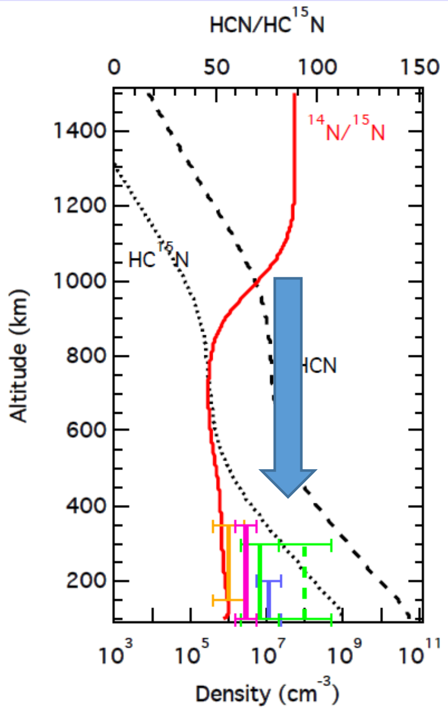


Possible ↗ of $^{14}N/^{15}N$ at high southern latitude due to air subsidence in 2012-2015.



Vinatier et al. (2020)



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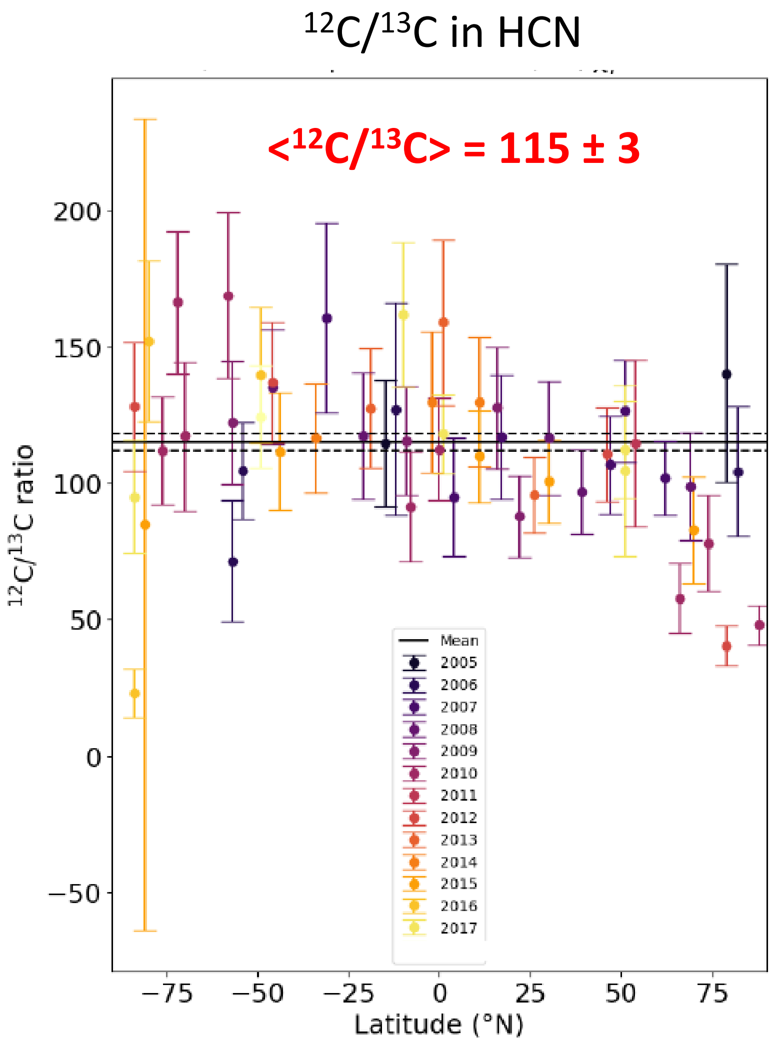
$^{12}C/^{13}C$ in HCN: results from CIRS data between 2005 and 2017



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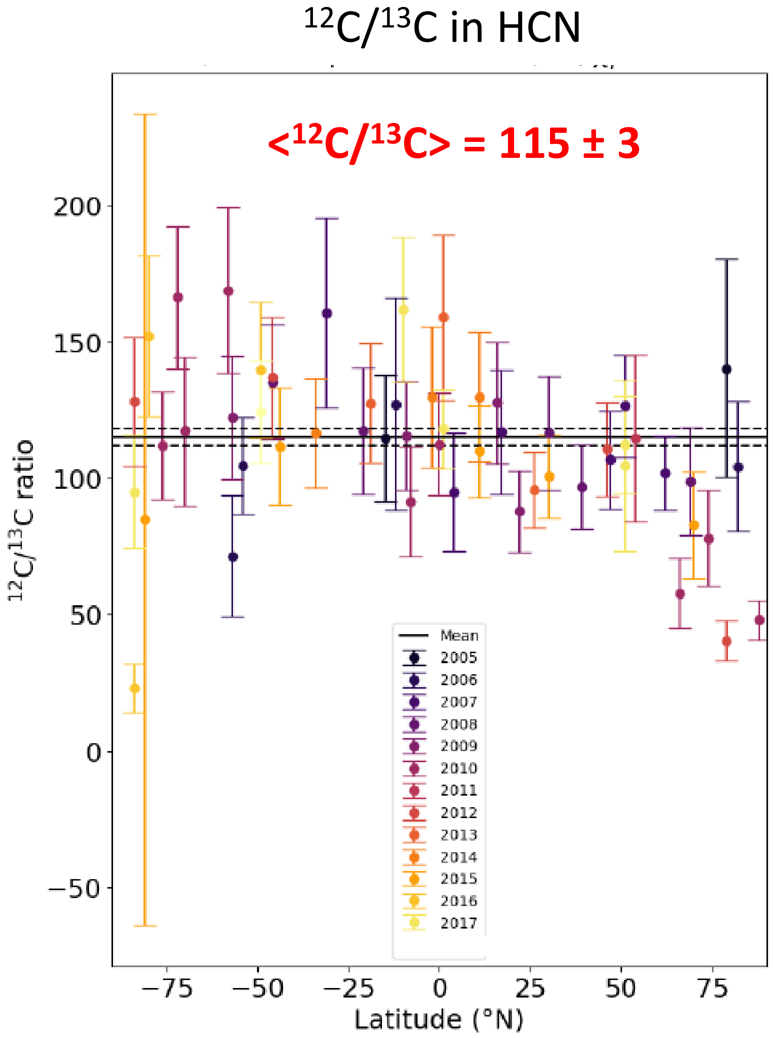

$^{12}C/^{13}C$ in HCN previous measurements:

- Disk-averaged

108 ± 20	SMA	*Gurwell et al. (2004) A*
132 ± 25	SMA	*Gurwell et al. (2004) D*
96 ± 13	Herschel/SPIRE	*Courtin et al. (2011)*
66 ± 35	Herschel/PACS	*Rengel et al. (2014)*
89.8 ± 2.8	ALMA	*Molter et al. (2016)*

- Spatially resolved

89 ± 20 at 15°S
68 ± 20 at 83°N

Cassini/CIRS, 2005 *Vinatier et al. (2007)*

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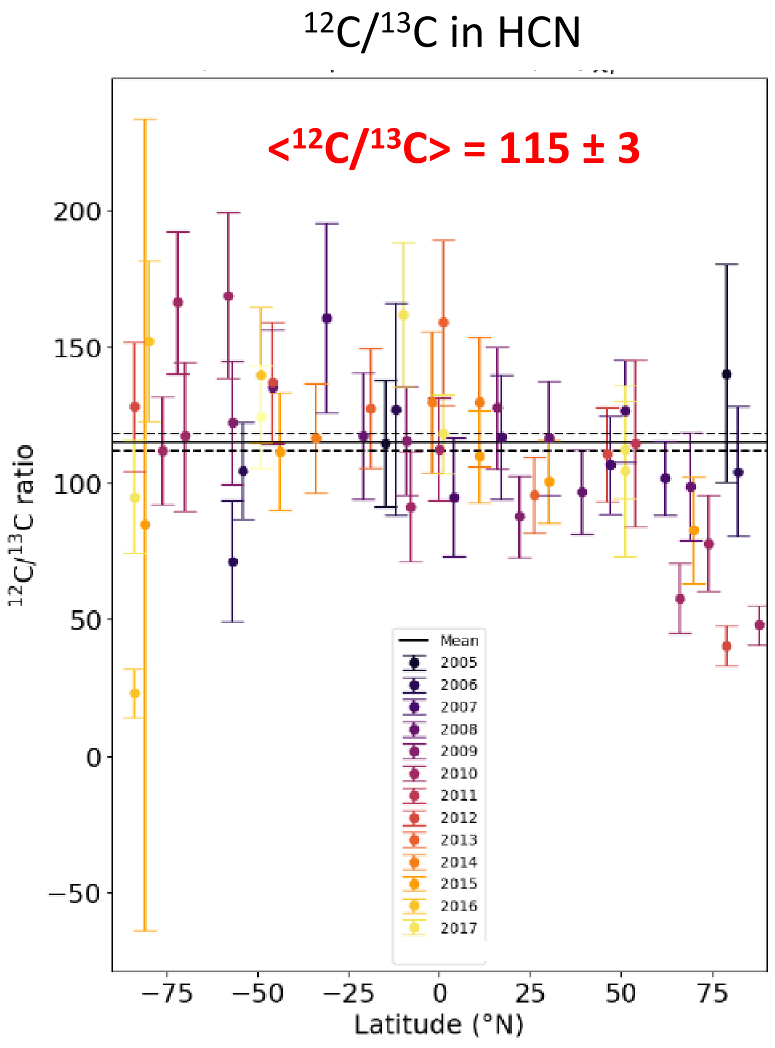

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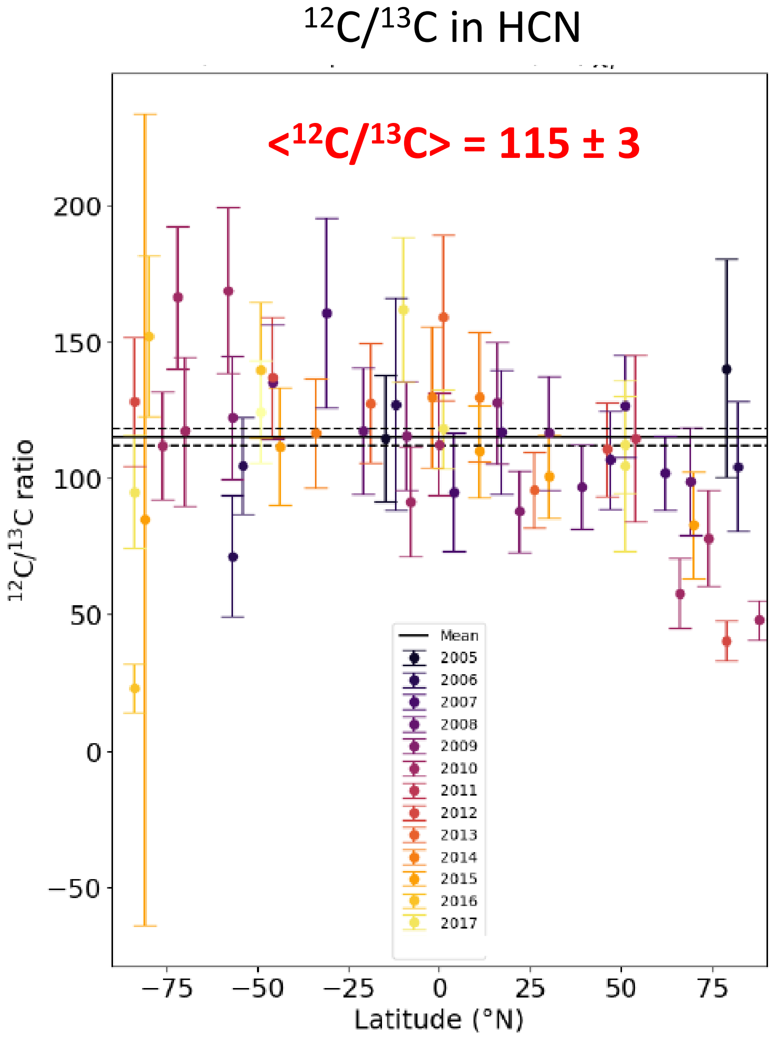
$^{12}C/^{13}C$ in CH_4 = 91.1 ± 1.4, in situ GCMS (*Niemann et al., 2010)*

$^{12}C/^{13}C$ is not considered in photochemical models as no fractionation is expected.

$^{12}C/^{13}C$ in HCN: results from CIRS data between 2005 and 2017



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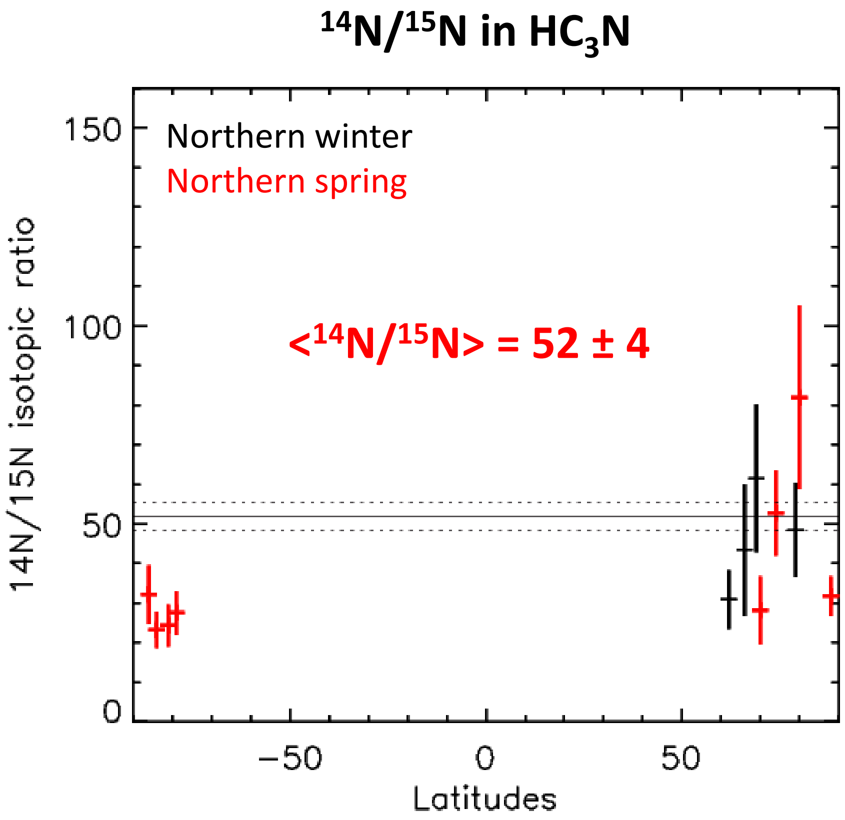
$^{12}C/^{13}C$ is not considered in photochemical models as no fractionation is expected.

⇒ Unknown fractionation process that increases ^{12}C and/or reduces ^{13}C in HCN ?

Possible $\searrow$ of $^{12}C/^{13}C$ from southern hemisphere to northern hemisphere.

$^{14}N/^{15}N$ in HC_3N: results from CIRS data between 2005 and 2017



Previous $^{14}N/^{15}N$ measurement in HC_3N
Disk-averaged:

$^{14}N/^{15}N = 67 \pm 14$ ALMA, *Cordiner et al. (2018)*

In agreement with ALMA disk-averaged observations.

$^{14}N/^{15}N$ is smaller in HC_3N than in HCN.

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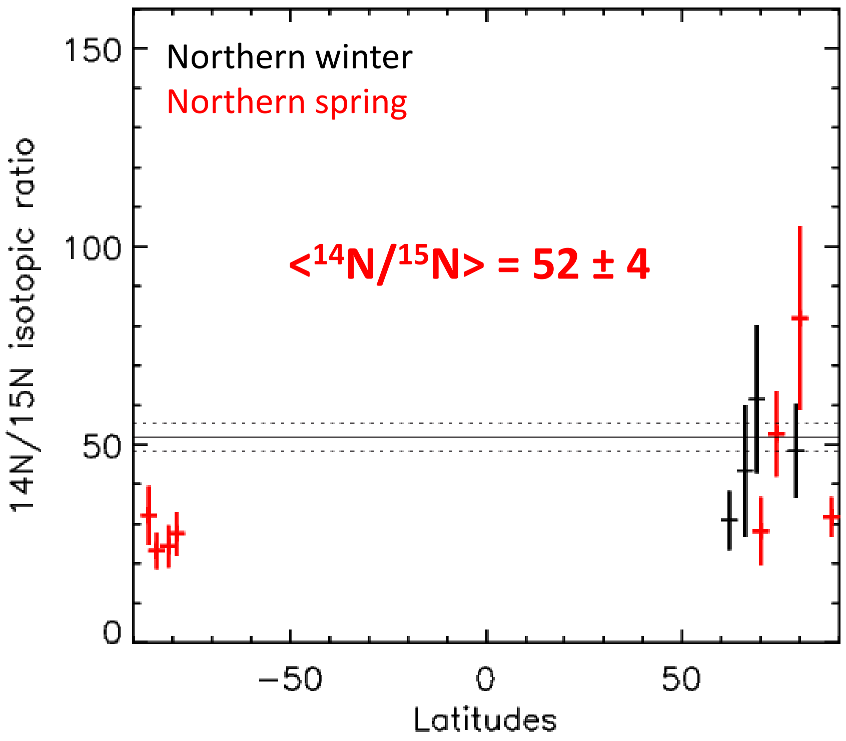

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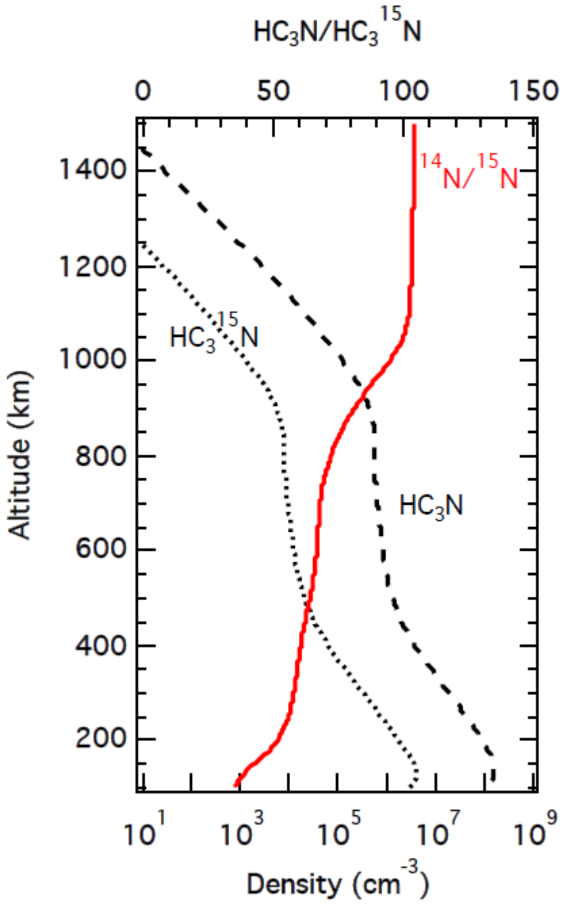
In agreement with photochemical model predictions at 200 km (Vuitton et al., 2019).



Vuitton et al. (2019)

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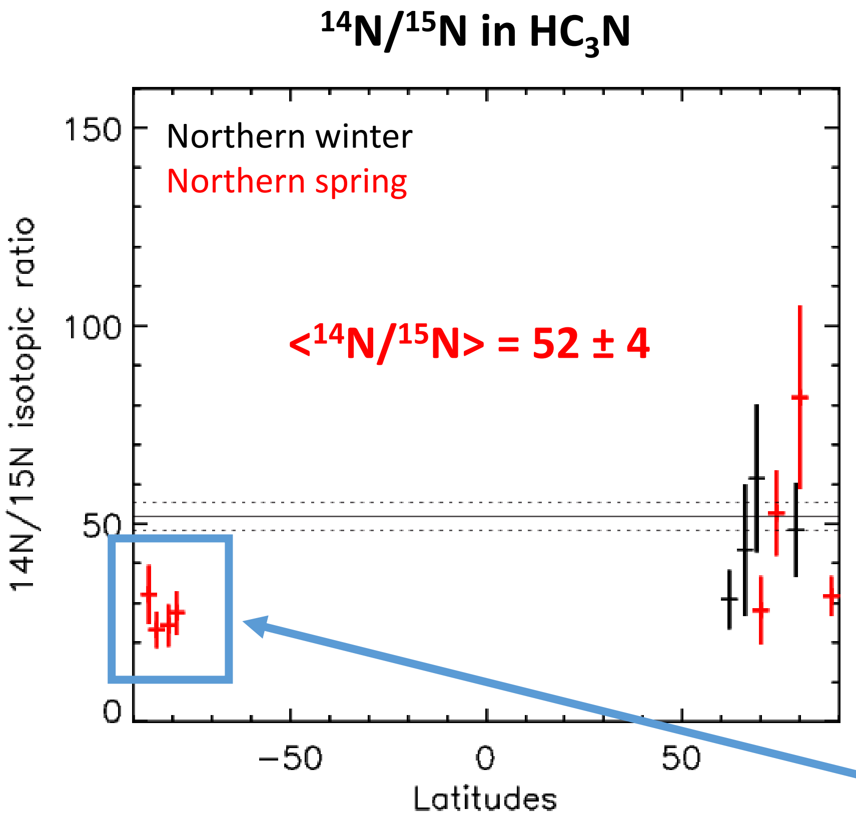

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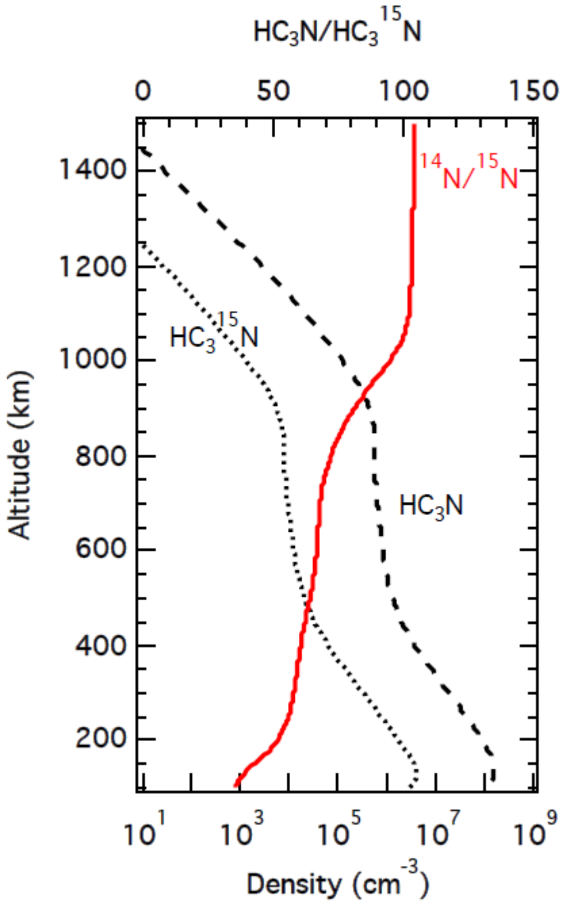
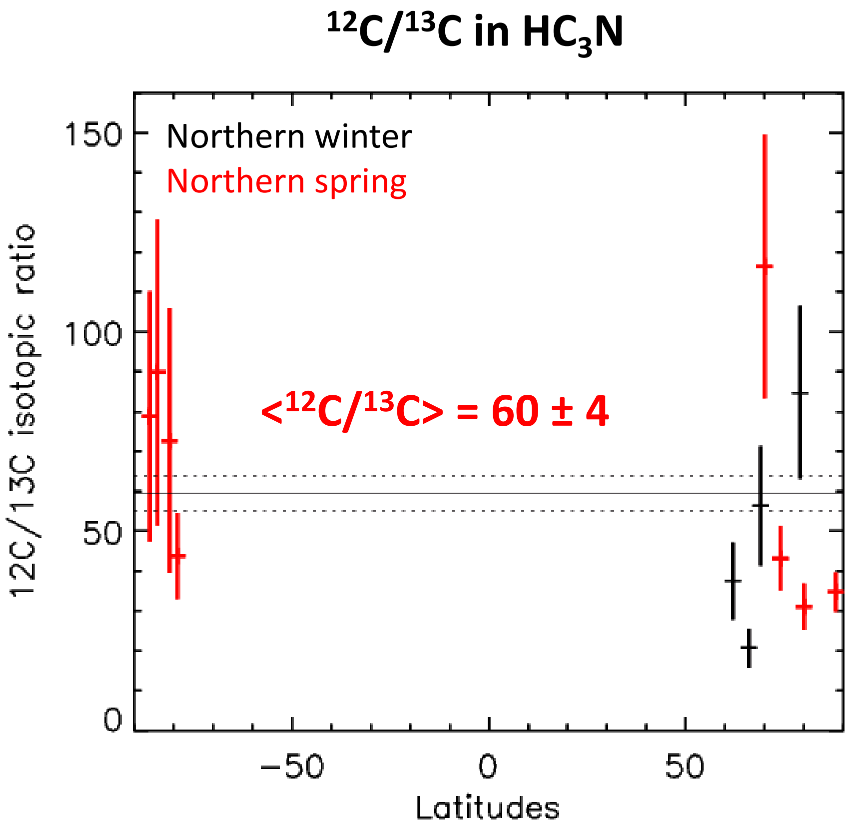
Possible $^{14}N/^{15}N$ depletion in the Southern polar vortex since 2015.
-> surprising as increase of $^{14}N/^{15}N$ would be expected from subsidence on increasing-with-height $^{14}N/^{15}N$ profile.



Vuitton et al. (2019)

$^{12}C/^{13}C$ in HC_3N: results from CIRS data between 2005 and 2017



Previous $^{13}C/^{12}C$ measurement in HC_3N
Spatially resolved:
$^{12}C/^{13}C = 79 \pm 17$ Cassini/CIRS in 2006-2007, *Jennings et al. (2008)*

Agreement with previous CIRS results.

No latitudinal nor temporal variations seems to be observed.

$^{12}C/^{13}C$ in HC_3N is about twice smaller than in HCN.

^{13}C isotope is currently not taken into account in photochemical models.
=> could help to identify some fractionation process in the nitrile photochemistry.

Conclusions

We derived the $^{14}N/^{15}N$ and $^{12}C/^{13}C$ isotopic ratios in HCN and HC_3N using the entire Cassini/CIRS dataset.

$^{14}N/^{15}N$ isotopic ratio

- in HCN : 68 ± 2
- in HC_3N : 52 ± 4

-> fractionation process in the formation of both nitriles.

-> in agreement with photochemical model predictions (Vuitton et al. 2019, Dobrijevic et al. 2018)

Possible latitudinal variations in the southern polar vortex in autumn.

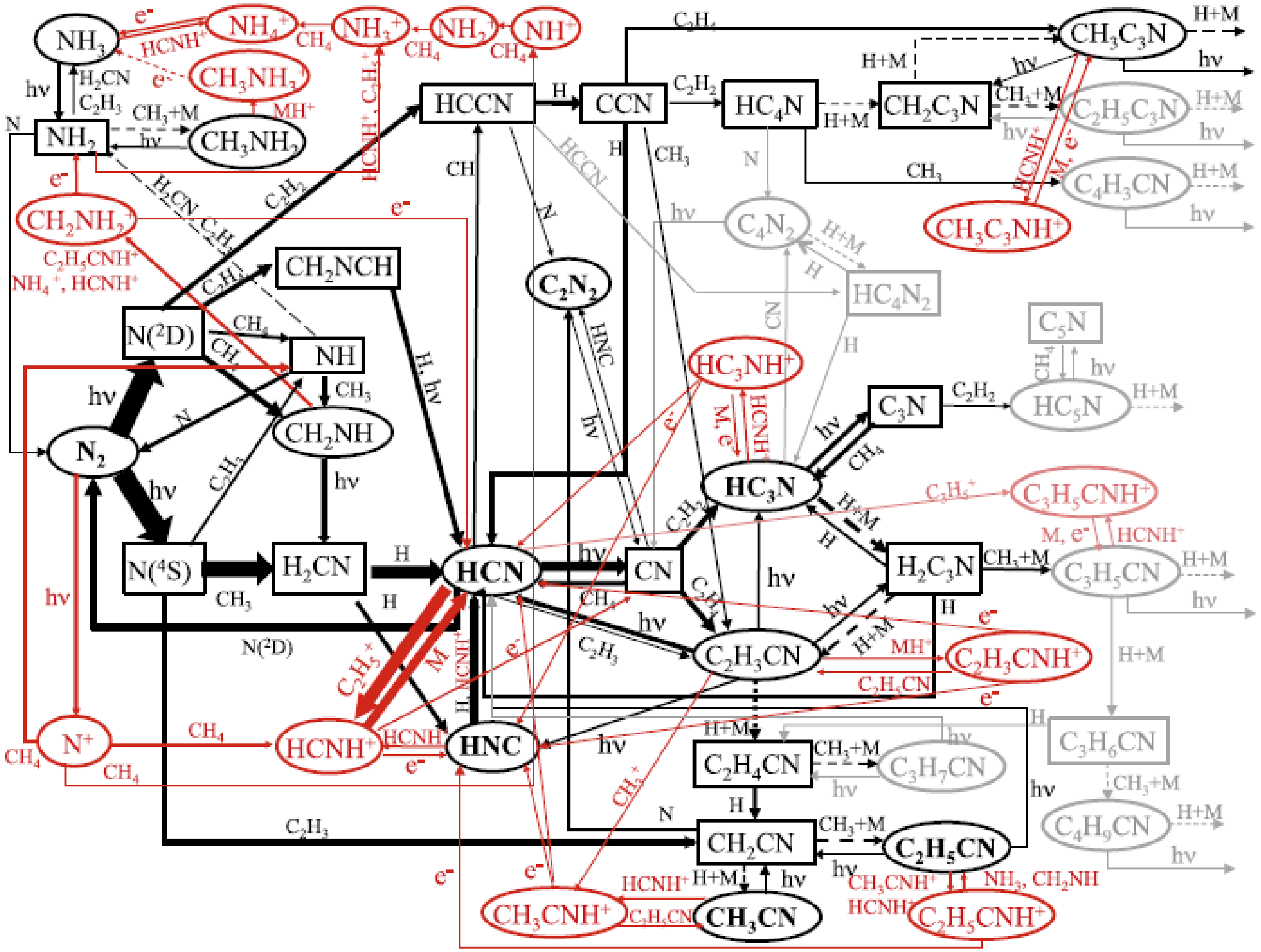
$^{12}C/^{13}C$ isotopic ratio

- in HCN : 115 ± 3
- in HC_3N : 60 ± 4

Both nitriles show different $^{12}C/^{13}C$ ratios than in CH_4 (~90, and other hydrocarbons) => unknown fractionation process.

Possible $\searrow$ of $^{12}C/^{13}C$ from southern hemisphere to northern hemisphere.

1D photochemical model of Dobrijevic et al. (2016)

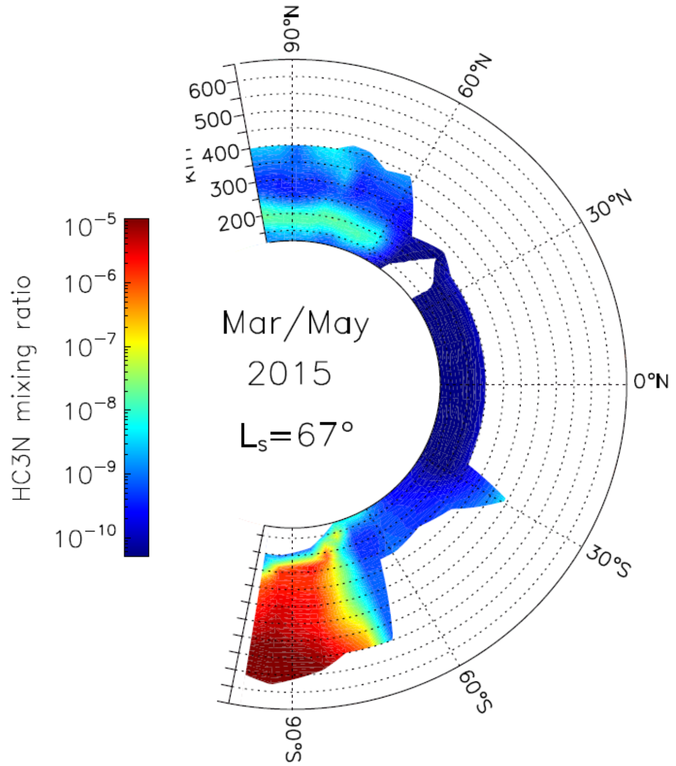


Important neutral pathways are in black.
Important ionic pathways are in red. Detected molecules are in bold.

HC_3N latitudinal distribution in 2015

HC_3N is detected in the polar region with high SNR as it is enriched by the global dynamics subsidence.

HC_3N mixing ratio in May 2015



Vinatier et al., (2020)