Nitrogen Fractionation and Formation of the Solar System

Steven Charnley

NASA Goddard Space Flight Center

Nitrogen Fractionation in Space

Niels Bohr Institute/ Danish Natural History Museum

November 8 2017

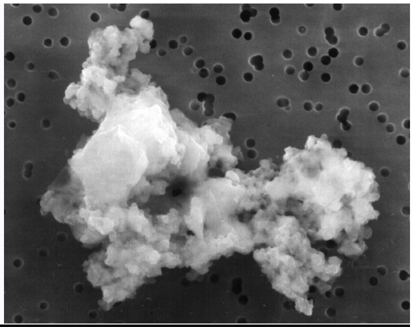
ACKNOWLEDGEMENTS

Eva Wirstroem, Gilles Adande, Stefanie Milam

OVERVIEW

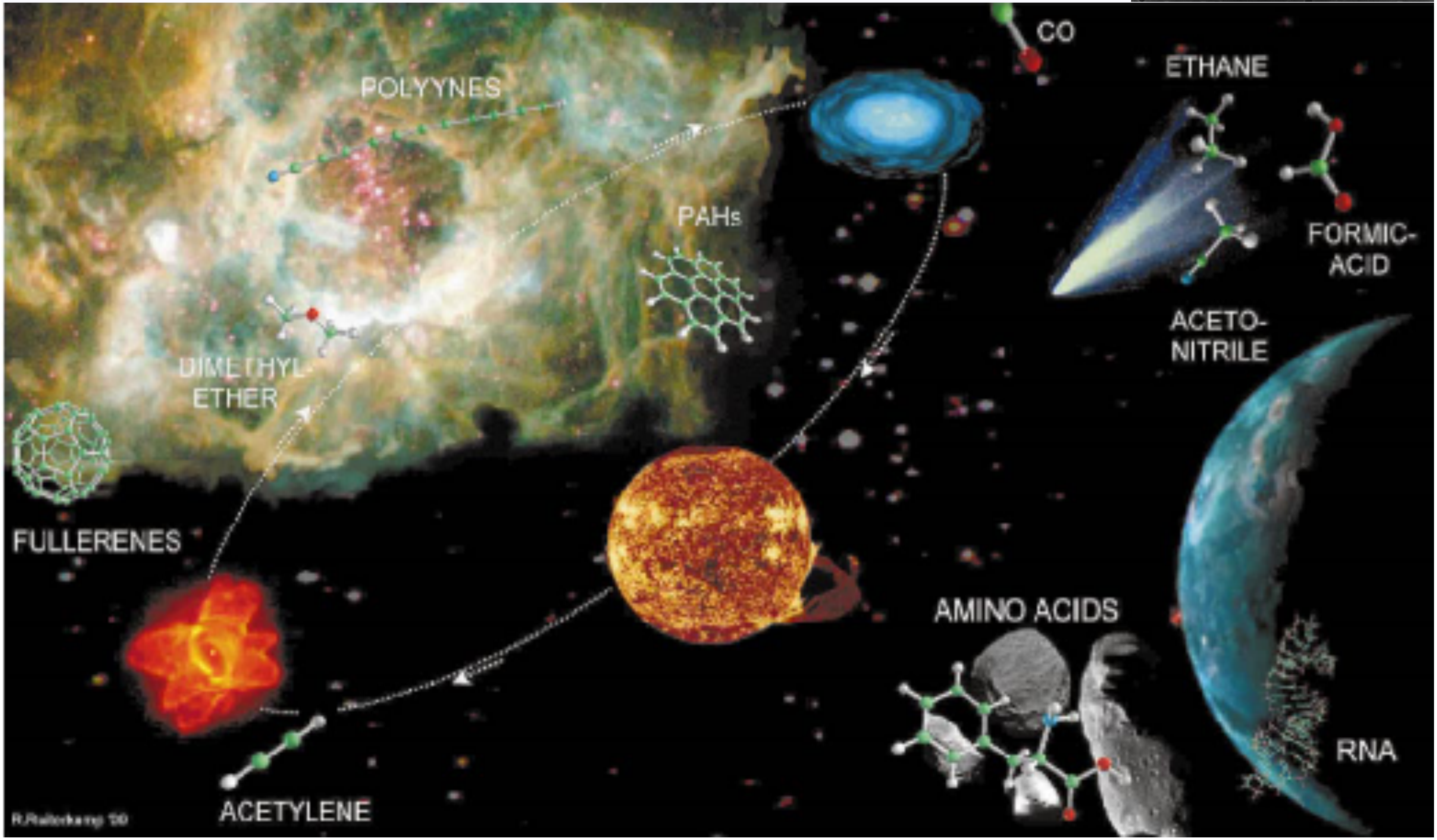
- $^{14}N/^{15}N$ ratios and Solar System
- Comets & meteorites: evidence for an ISM link?
- Interstellar ^{15}N fractionation: models and observations
- Summary and current issues

ISM-Solar System Isotopic Connection?



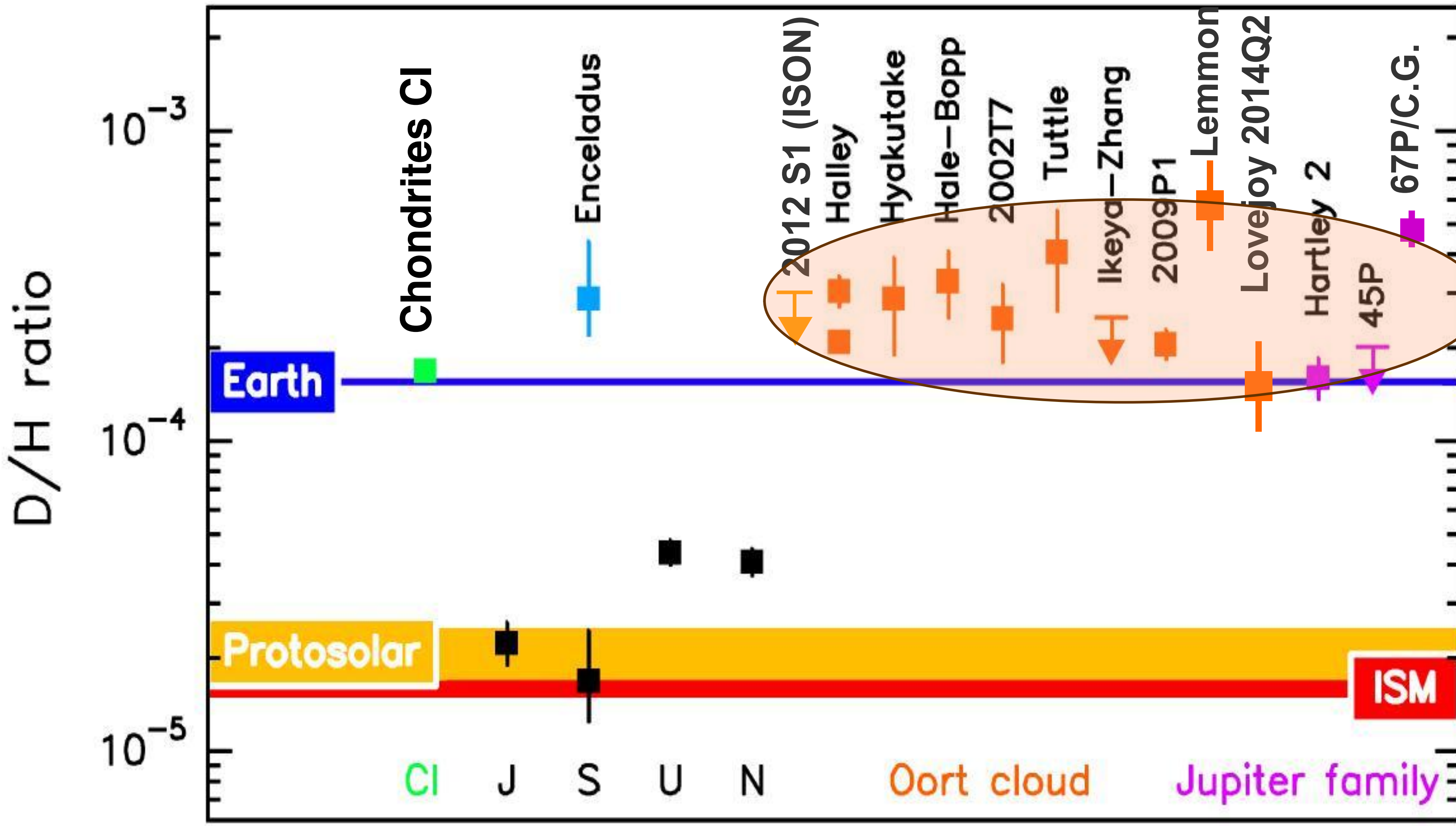
Primitive material = comets, asteroids, meteorites, IDPs

Isotopic fractionation a remnant of cold interstellar chemistry ?



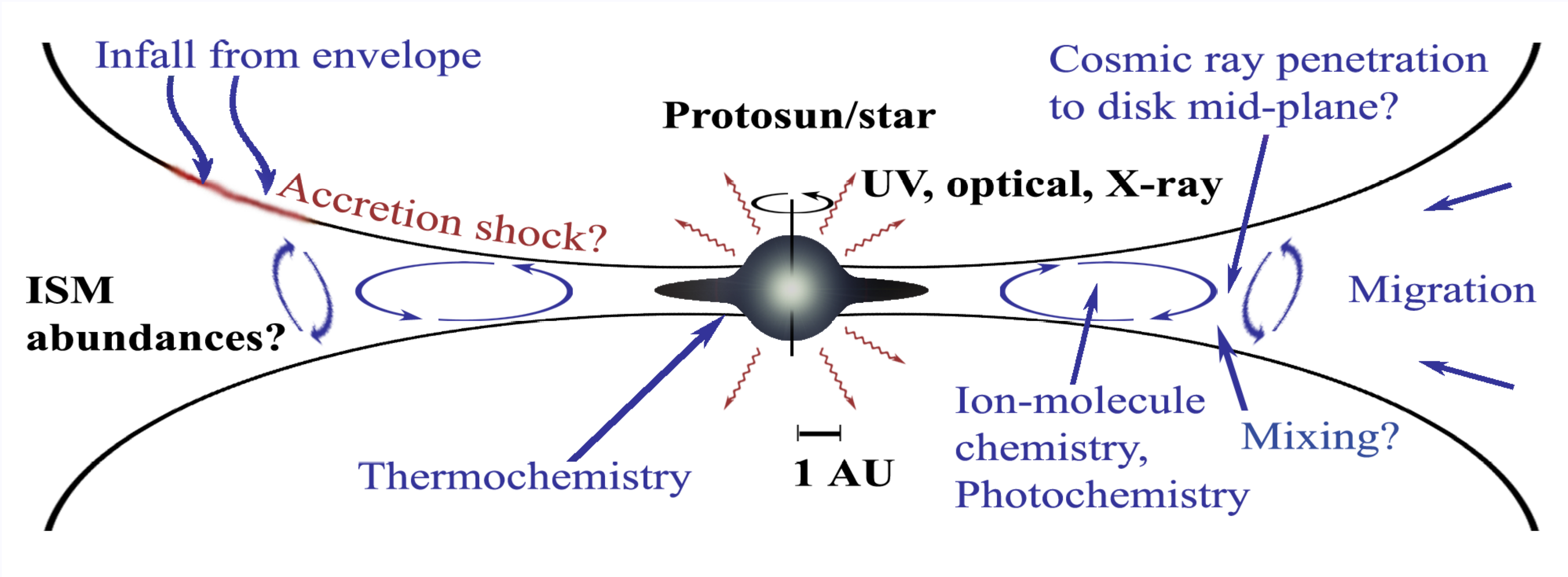
D/H IN THE SOLAR SYSTEM

Cometary water

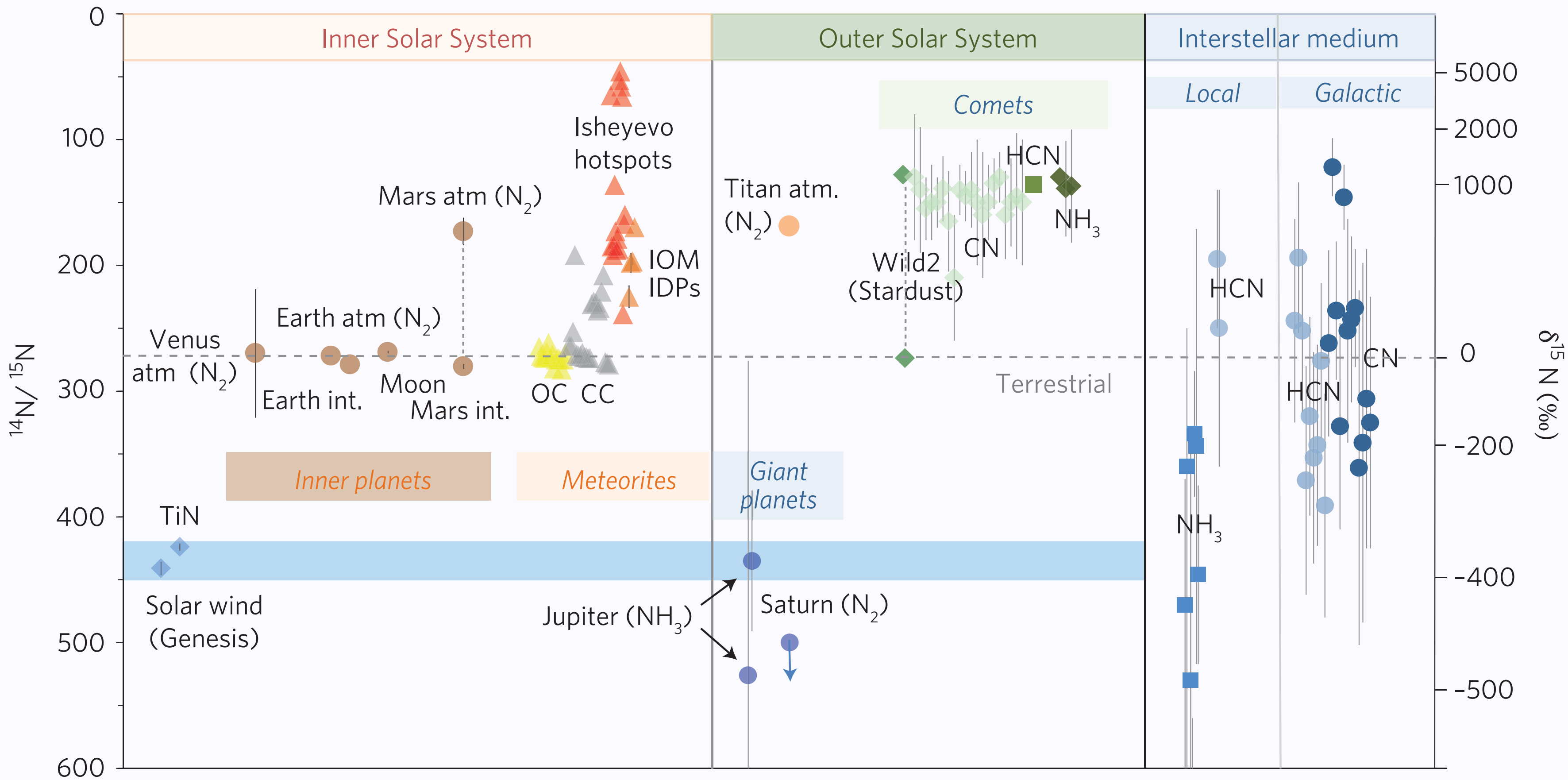


Adapted from Lis et al. (2013)

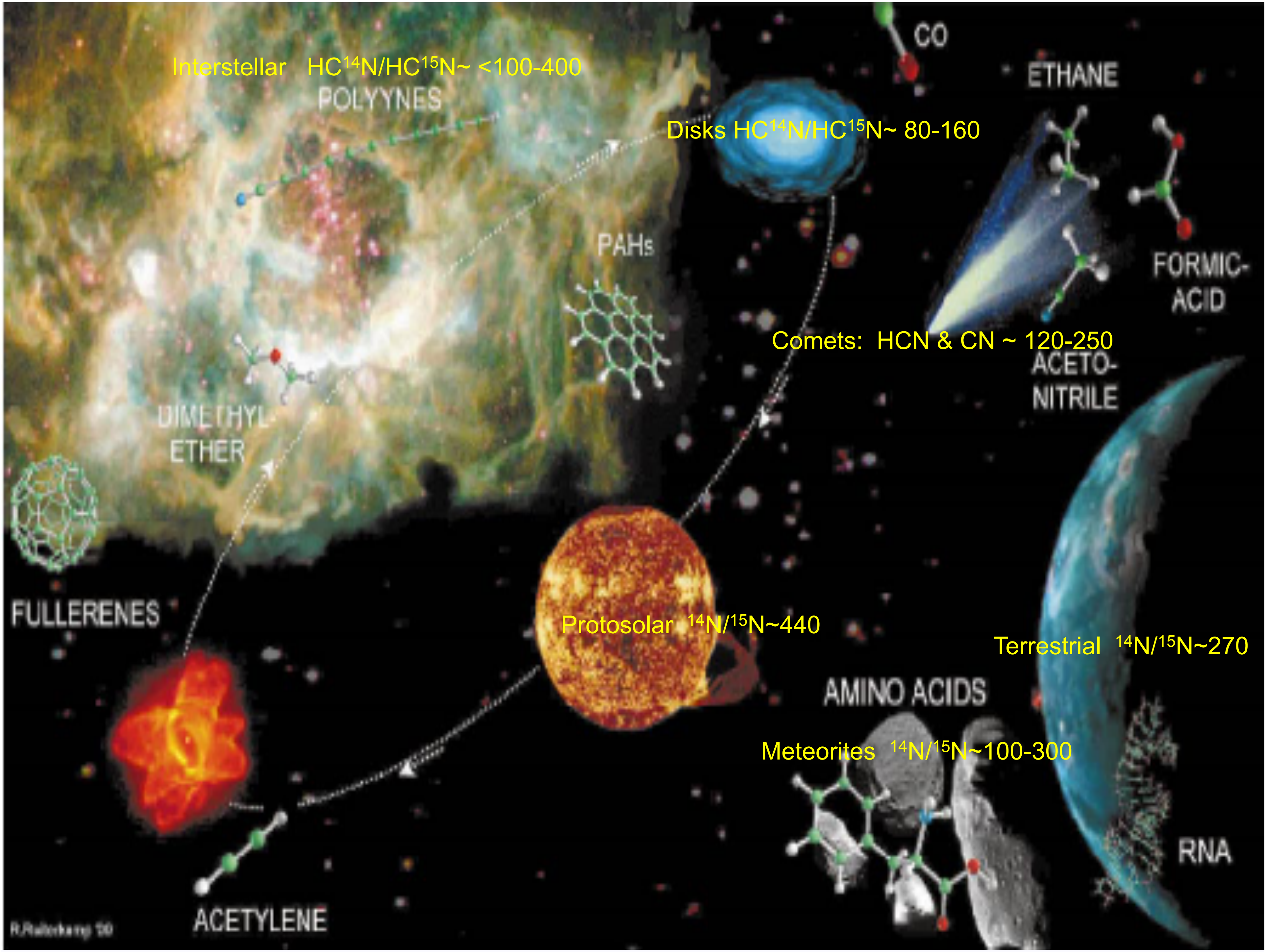
Processes affecting ISM fractionation in Proto-planetary Disks



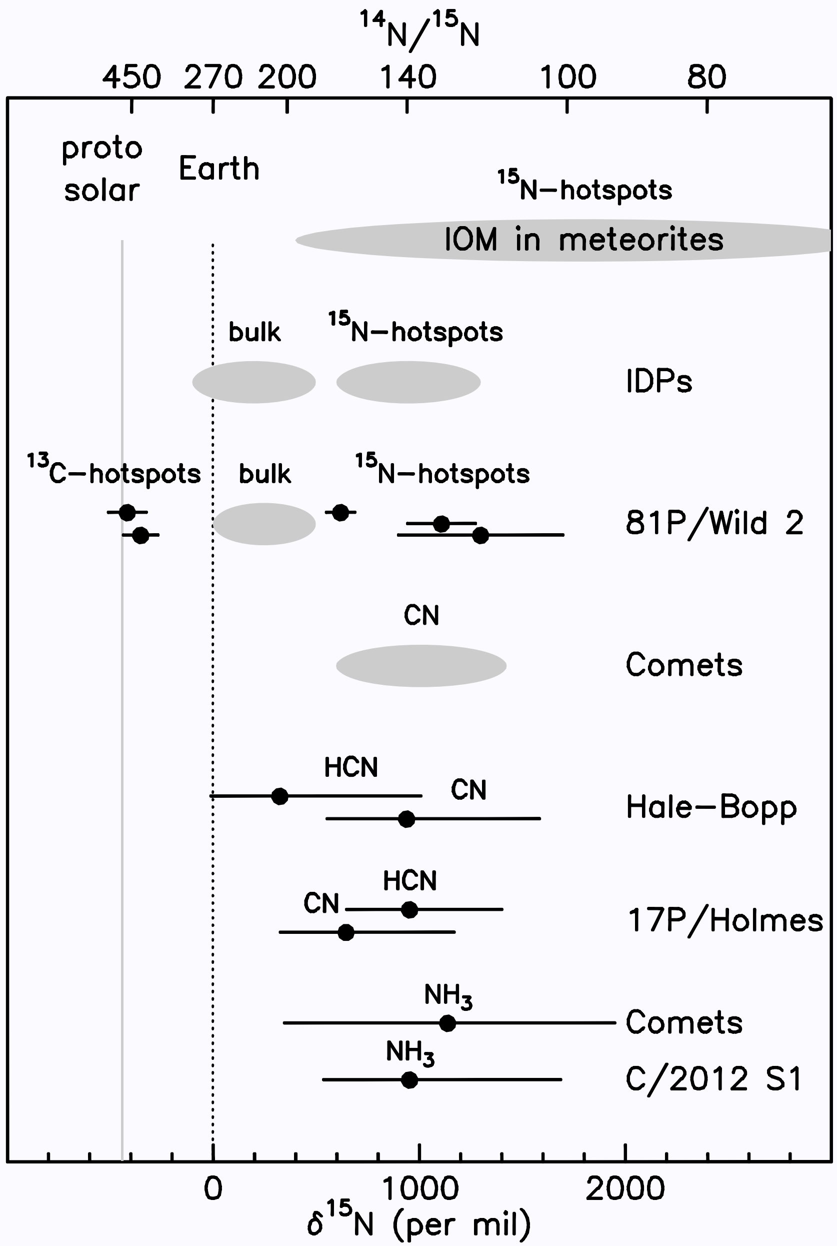
Nitrogen Isotopes in Solar System Objects



Fueri & Marty (2015)

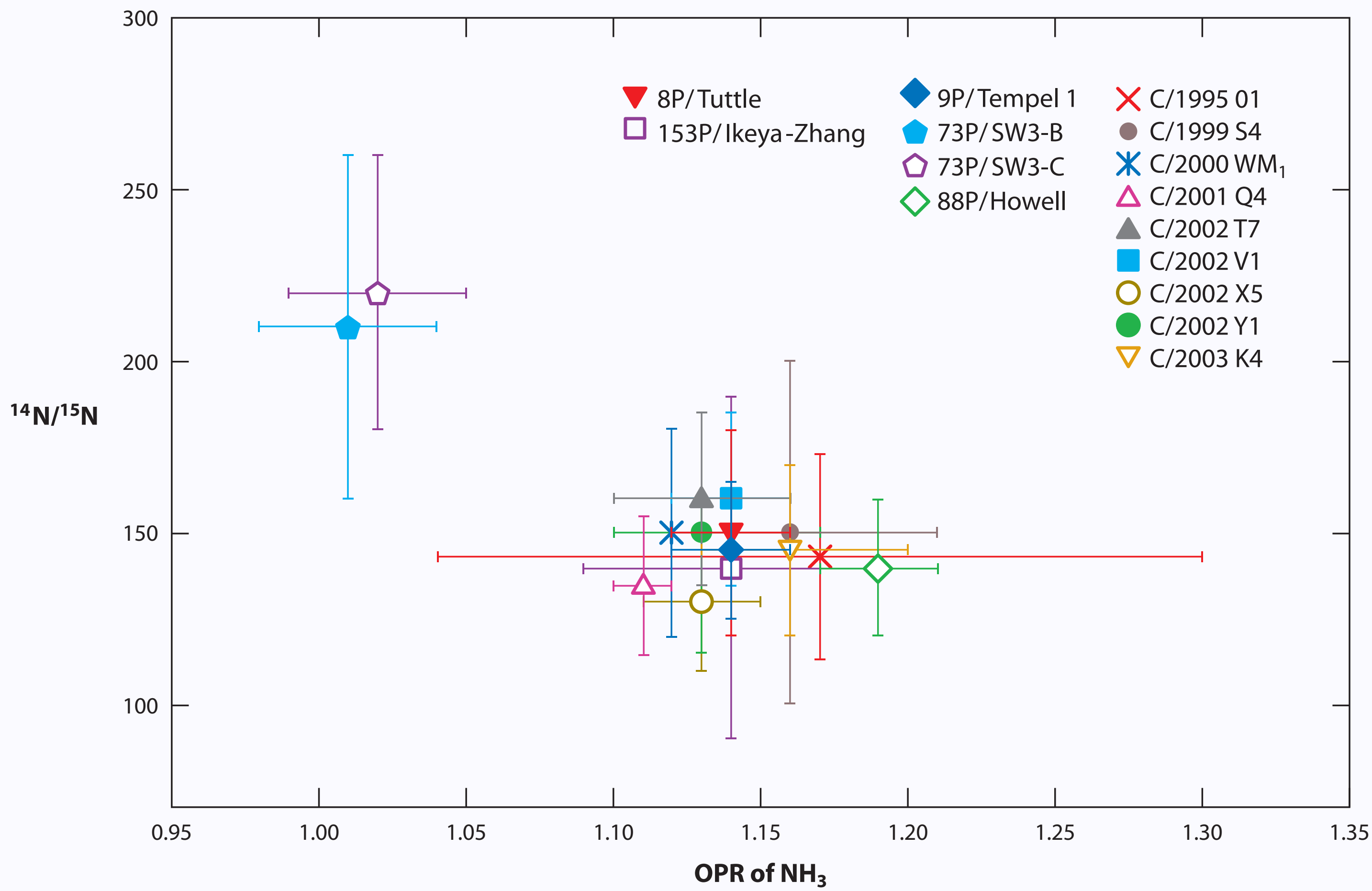

Interstellar HC^{14}N/HC^{15}N~ <100-400
POLYYNES
CO
ETHANE
Disks HC^{14}N/HC^{15}N~ 80-160
PAHs
FORMIC-
ACID
Comets: HCN & CN ~ 120-250
ACETO-
NITRILE
DIMETHYL
ETHER
FULLERENES
Protosolar ^{14}N/^{15}N~440
Terrestrial ^{14}N/^{15}N~270
AMINO ACIDS
Meteorites ^{14}N/^{15}N~100-300
RNA
ACETYLENE

$^{14}N/^{15}N$ in the Solar System



Bockelee-Morvan et al. (2015)

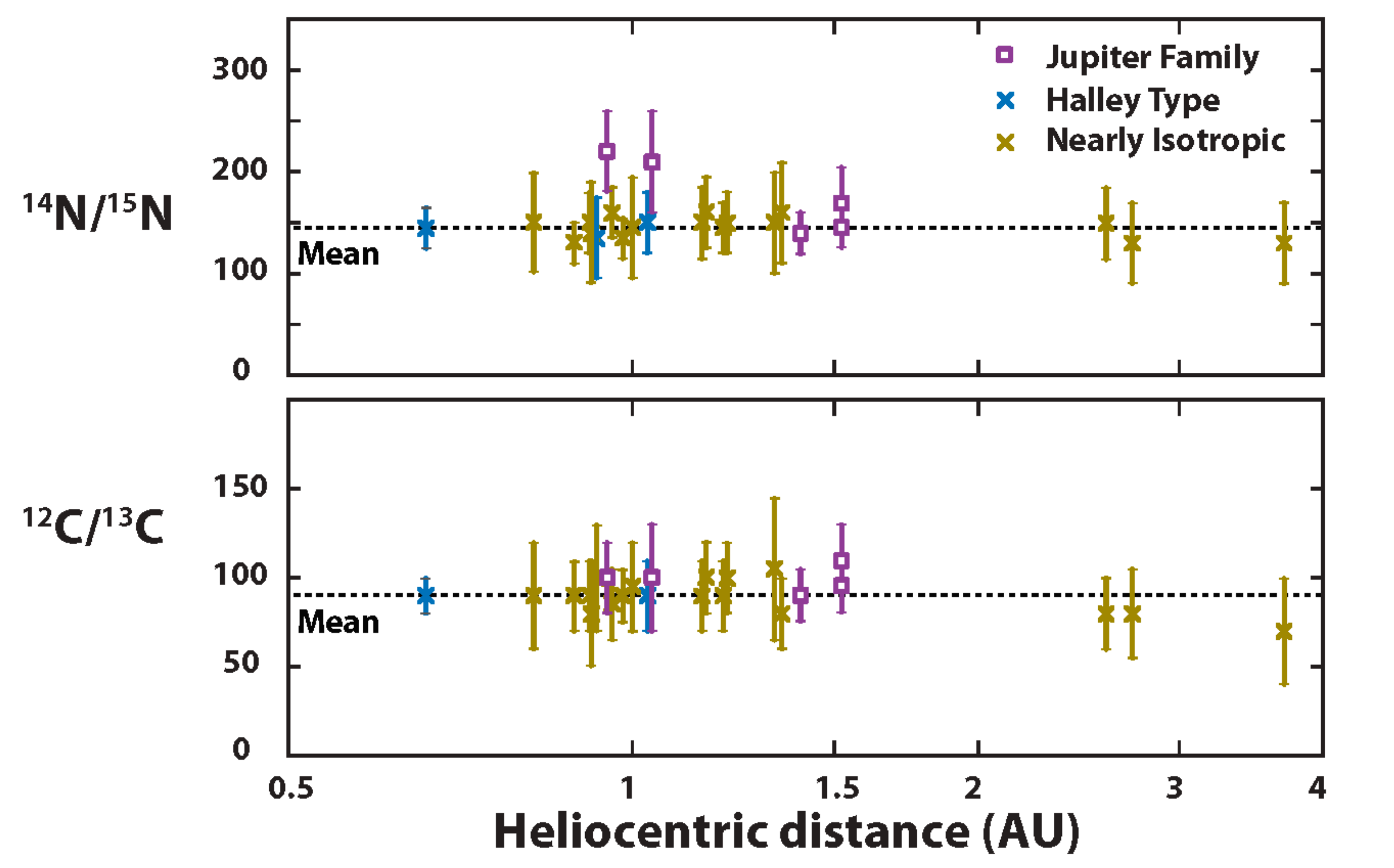
$C^{14}N/C^{15}N$ in Comets: Oort Cloud & JFCs



Adapted from Shinnaka et al. (2011)

Isotopes of Nitrogen and Carbon in Comets: CN

Adapted from Manfroid et al. 2009



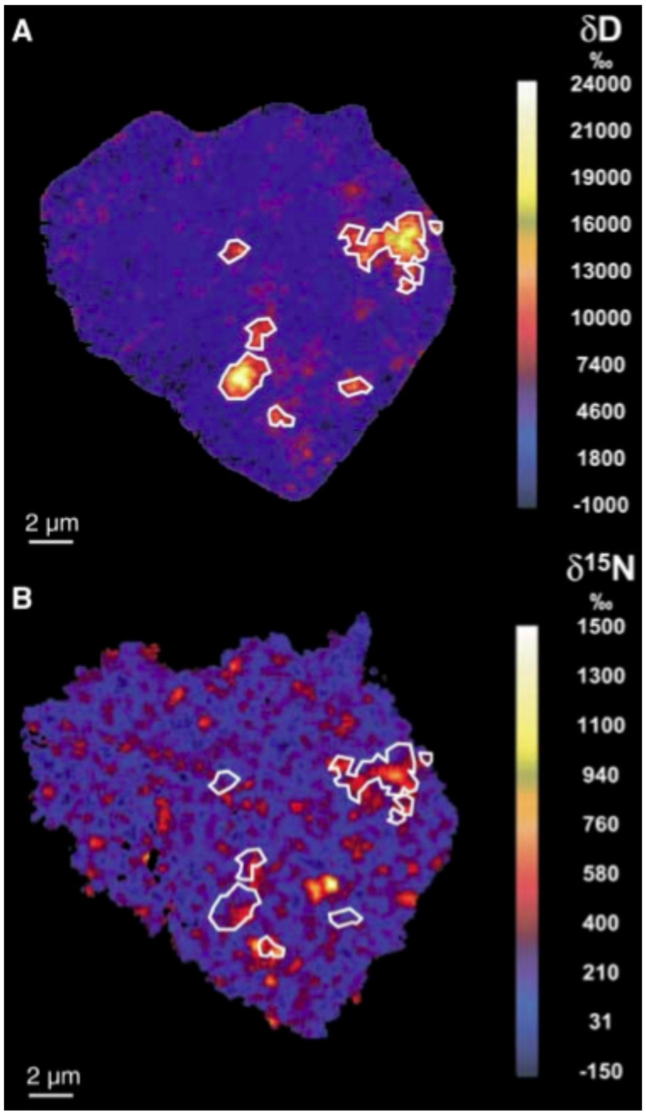
Nebular vs. Interstellar?

Levison et al. (2010): ~90% of Oort Cloud comets captured from stars in Sun's birth cluster?

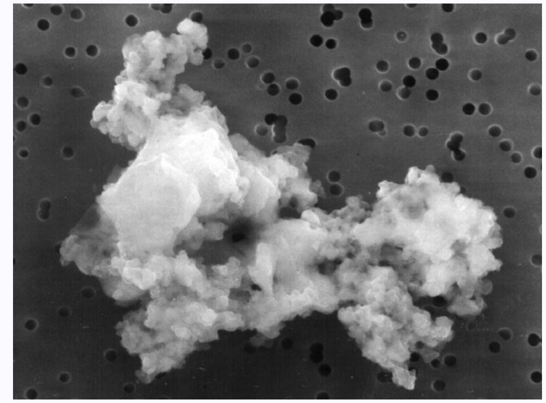
^{15}N Fractionation in Meteorites

PROTOSOLAR $^{14}N/^{15}N$~440

TERRESTRIAL $^{14}N/^{15}N$~270



Busemann et al. (2006)



Meteorites & IDPs:

`hotspots':

$^{14}N/^{15}N$~50-170 + D-rich

D-rich + ^{15}N-poor

^{15}N-rich + D-poor

Duprat et al. (2014)
Van Kooten et al. (2017)

Present in the Insoluble and Soluble Organic Material

Problems: 1) origin of the fractionation?
2) nature of the carrier(s):
- nitrile or amine?
- aliphatic or aromatic?

Ion-Molecule Fractionation Chemistry

Dense, starless/prestellar cores
(n~10^5 cm^{-3}, T ~10K, CO depletion)

e.g. Barnard 68

(Lada et al. 2004)

$$^{15}N + {}^{14}N_2H^+ \rightleftharpoons {}^{14}N + {}^{15}N^{14}NH^+$$
$$\rightleftharpoons {}^{14}N + {}^{14}N^{15}NH^+$$

$$^{15}N + HC^{14}NH^+ \rightleftharpoons {}^{14}N + HC^{15}NH^+$$

$$^{15}N^+ + {}^{14}N_2 \rightleftharpoons {}^{14}N^+ + {}^{14}N^{15}N$$

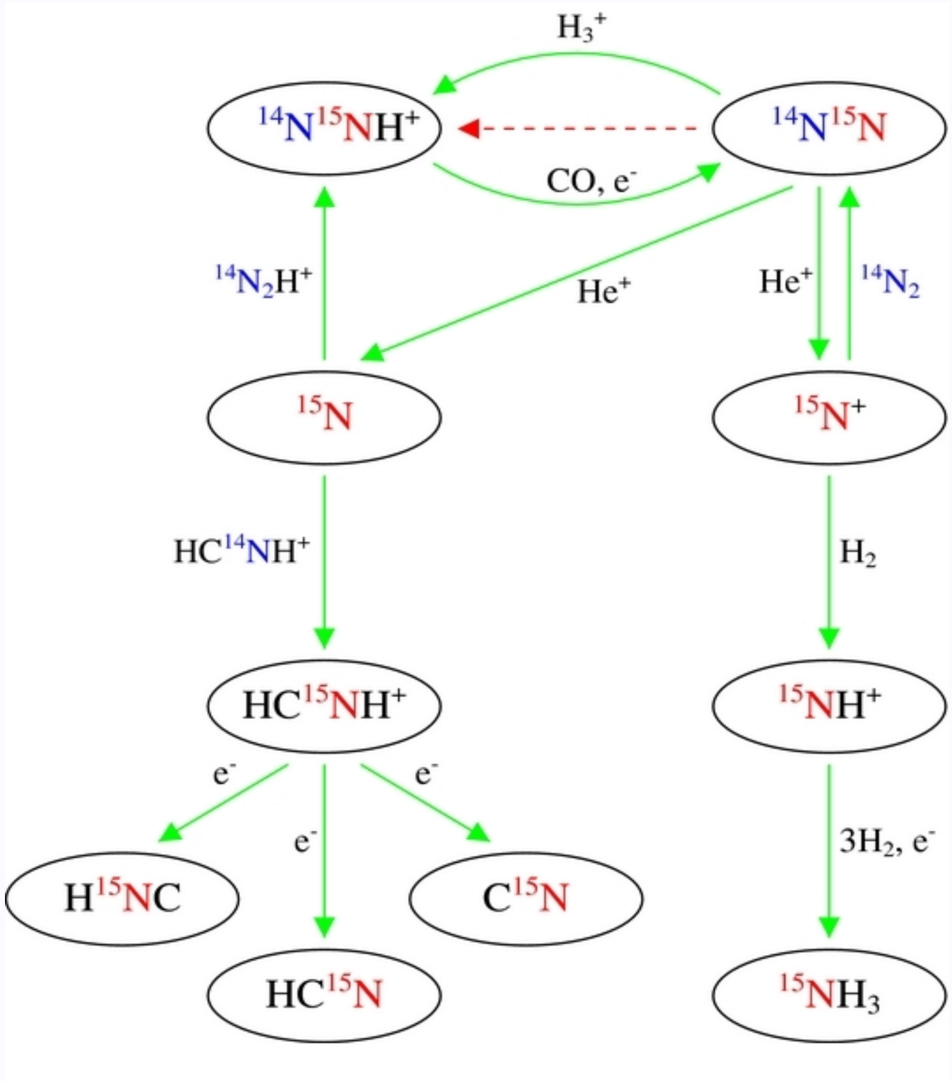
$$^{15}N + C^{14}NC^+ \rightleftharpoons {}^{14}N + C^{15}NC^+$$

Terzieva & Herbst (2000)

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2$$
$$H_2D^+ + HD \rightleftharpoons D_2H^+ + H_2$$
$$D_2H^+ + HD \rightleftharpoons D_3^+ + H_2$$

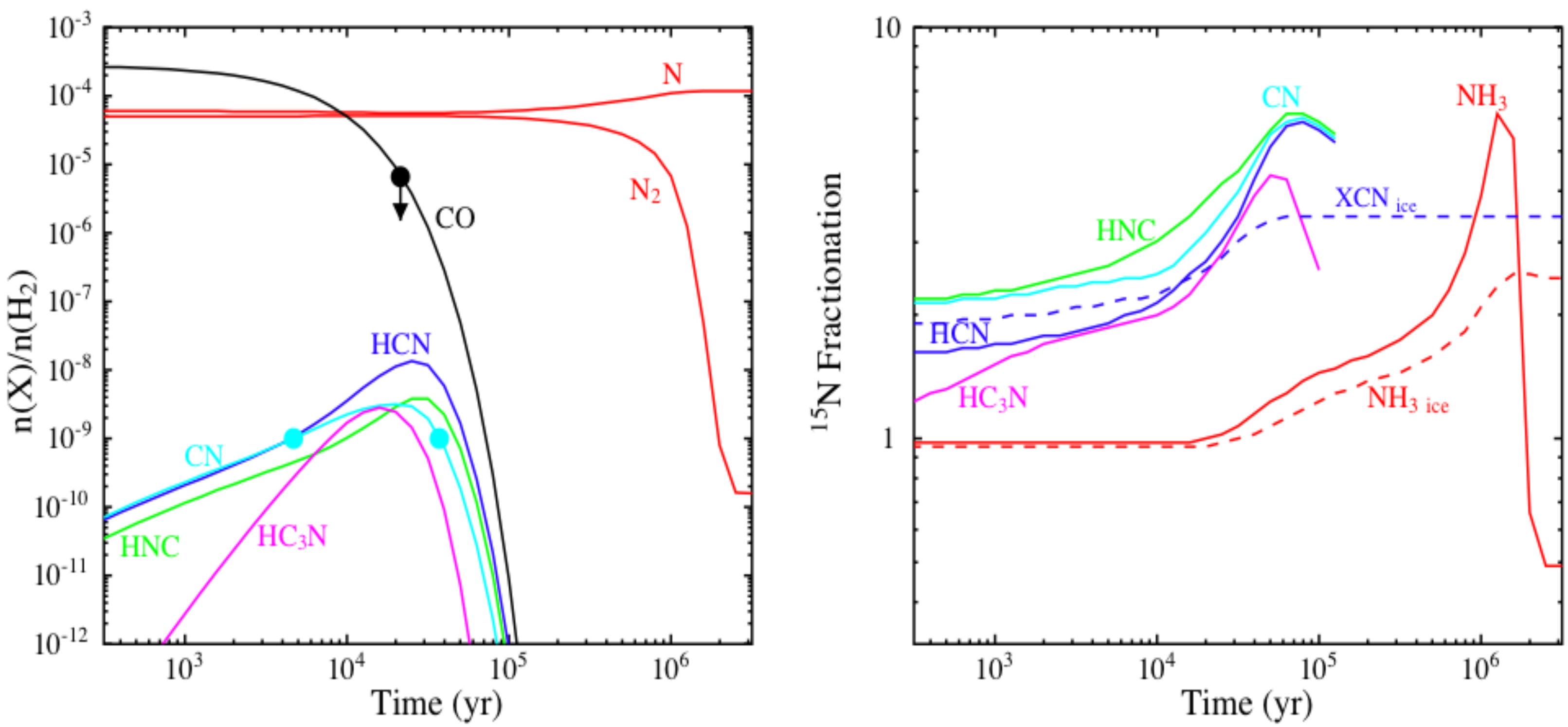
Roberts et al. (2003)

Interstellar ^{15}N Chemistry



Terzieva & Herbst (2000); Wirstrom et al. (2012)

^{15}N Fractionation – Two Routes



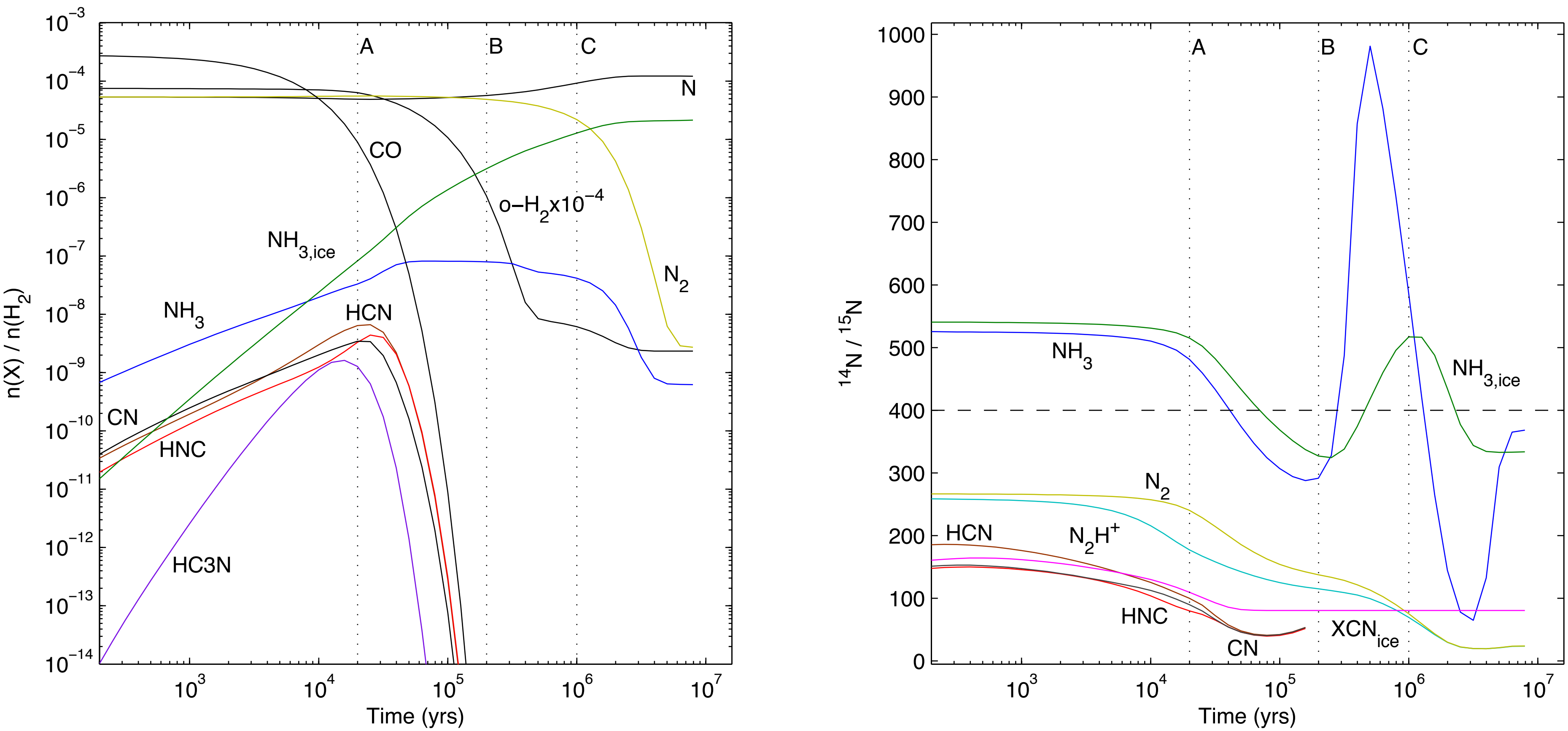
Requires high initial atomic N abundance and

$$N + CN \not\longrightarrow C + N_2$$

Rodgers & Charnley (2008)
Hily-Blant et al. (2013)

Interstellar Origin for Cometary $^{14}N/^{15}N$ Ratios ?

Necessary if ~90% of Oort Cloud comets from extrasolar systems (Levison et al. 2010) and/or outer Solar nebula shielded from cosmic rays (Cleeves et al. 2014).



Wirstroem et al. (2012)

An ion-molecule origin for $^{14}N/^{15}N$ ratios in the ISM?

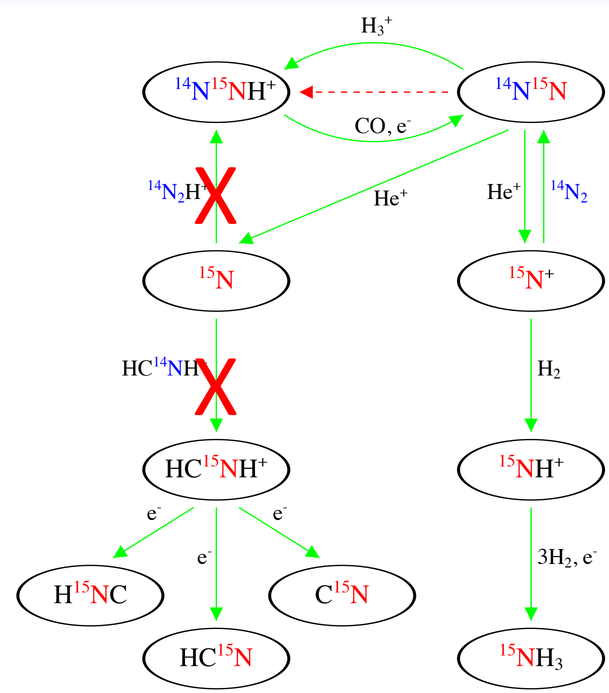
- $^{14}N/^{15}N$ nitrile ratios most enriched as observed in ISM and comets
- Low ^{15}N enrichment/depletion in interstellar NH_3 possibly a time-dependent effect
- Depletion of ^{15}N in N_2H^+ a problem - models only predict ISM enrichment
- Observed ^{15}N enrichment in *cometary* NH_3 not reproduced
- Roueff et al. (2015) calculate barriers for the key processes:

$$^{15}N + {}^{14}N_2H^+ \rightleftharpoons {}^{14}N + {}^{15}N^{14}NH^+$$
$$\rightleftharpoons {}^{14}N + {}^{14}N^{15}NH^+$$

$$^{15}N + HC^{14}NH^+ \rightleftharpoons {}^{14}N + HC^{15}NH^+$$

- Isotope-selective photodissociation of N_2 inefficient in dark cores (Heays et al. 2014); also in nebula?

- Models need to be re-evaluated (Wirstrom & Charnley 2017)



So, where are we?

- Growing database of cometary $^{14}N/^{15}N$ ratios in CN and NH_2 interspersed with a few HCN measurements

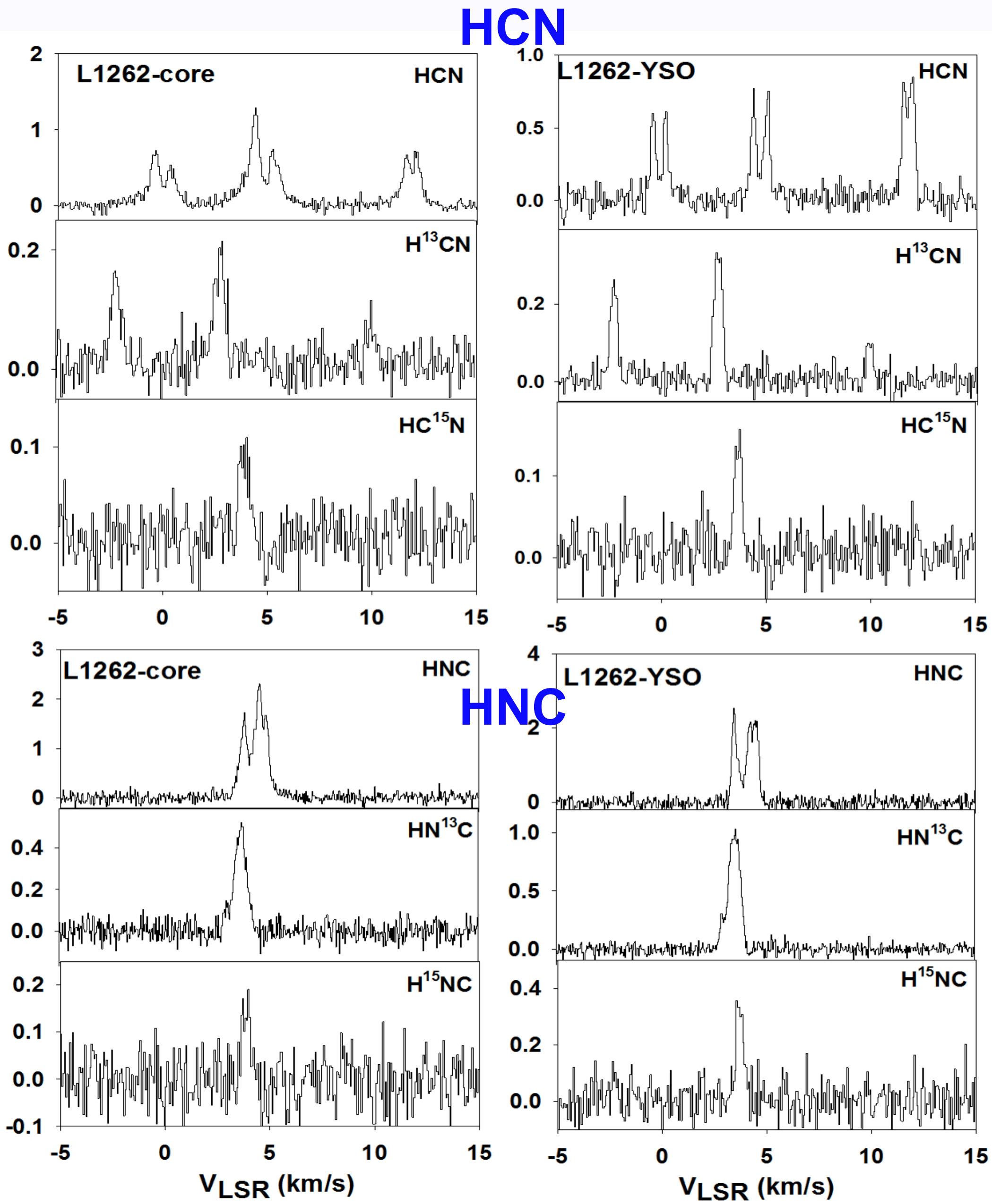
- Laboratory analyses demonstrating interesting correlations and anti-correlations in $^{14}N/^{15}N$ ratios wrt to enrichments, potential carriers, and to other isotopes (D).

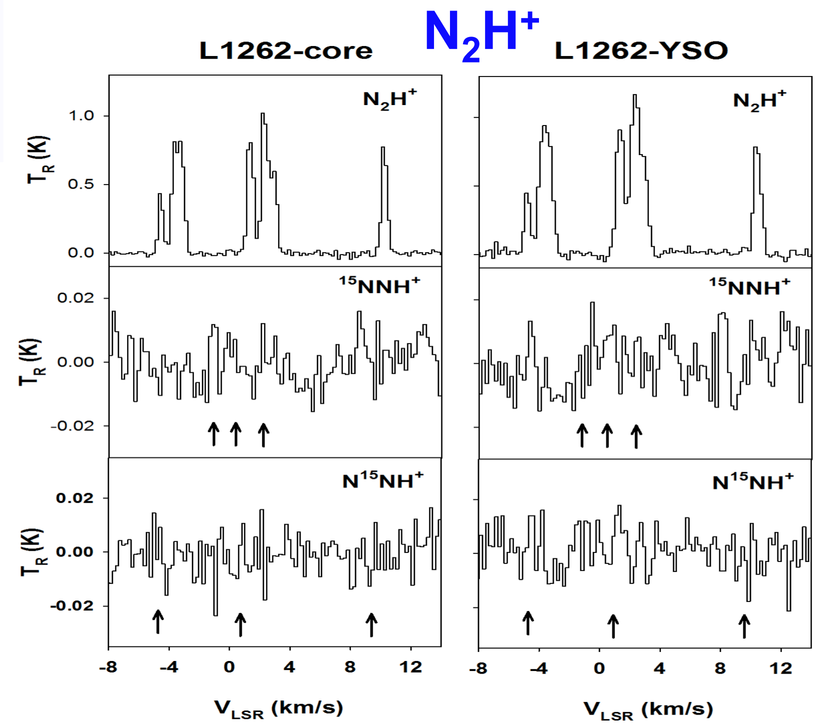
- Interstellar fractionation theory is in trouble.

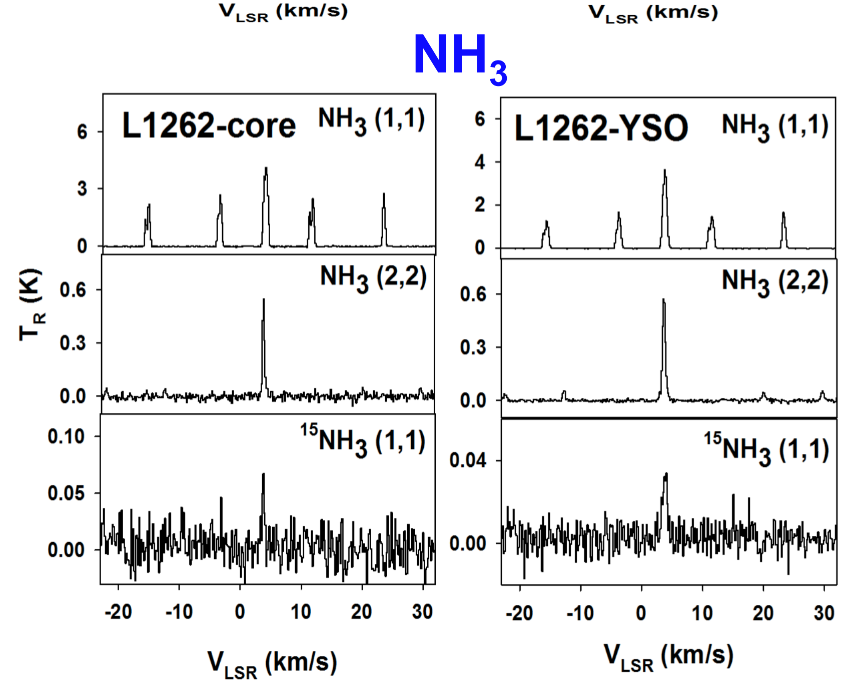
- We have a recent surge in astronomical observations of $^{14}N/^{15}N$ ratios in clouds and disks. Multi-molecular studies may provide insights into fractionation mechanisms

$^{14}N/^{15}N$ in Amines & Nitriles & N_2

Adande et al. (2017a & b)







$^{14}N/^{15}N$ Ratios in Dark Clouds circa 2010

Table 1: INTERSTELLLAR NITROGEN ISOTOPE RATIOS

Source	Type	NH_3	N_2H^+	HCN	HNC	Reference
L1544	dark core	...	446±71	261	>27	1,2,3
				69-154		3
L1498	dark core	...	...	>813	>90	4,3
				>75		3
L1521E	dark core	...	...	151±16	...	4
L1521F	dark core	...	...	>51	24-31	3,3
B1	protostar	334±50	...	...	...	5
NGC 1333	protostar	344±173	...	...	...	5
		350-850				6
Cha-MMS1	protostar	...	...	...	135	7

(1) Bizzocchi et al. (2010) (2) Hily-Blant et al. (2010) (3) This work (4) Ikeda et al. (2002) (5) Lis et al. (2010) (6) Gerin et al. (2009) (7) Tennekes et al. (2006)

Milam & Charnley (2010)

Observed $^{14}N/^{15}N$ Ratios in Molecular Clouds

TABLE 5
INTERSTELLAR NITROGEN ISOTOPE RATIOS

Source	Type	NH_3	$N_2H^{+\S}$	HCN	HNC	CN	Reference
L1544	dark core	>700	1000±200	**69-154**	**>27**	500±75	4,1,3,3,9
			1000±200	140-360			1,2
L1498	dark core	**619±100**	...	**>75**	**>90**	500±75	3,3,3,9
				>813			5
L1521E	dark core	...	...	151±16	...	...	5
L1521F	dark core	**539±118**	...	**>51**	**24-31**	...	3,3,3
L1262-core	dark core	**356±107**	**>450**	...	...	...	3,3
			>450				3
L183	dark core	$530\pm^{570}_{180}$	...	140-250	...	...	4,2
NGC 1333-DCO$^+$	dark core	$360\pm^{260}_{110}$	...	...	...	...	4
NGC 1333-4A	Class 0 protostar	344±173	...	...	...	...	6
		>270					4
B1	Class 0 protostar	300	>600	165	75	240	10,10,10,10,9
		334±50	400				6,10
L1689N	Class 0 protostar	$810\pm^{600}_{250}$	...	...	...	...	4
Cha-MMS1	Class 0 protostar	...	...	...	135	...	7
IRAS 16293A	Class 0 protostar	...	...	163±20	242±32	...	13
R Cr A IRS7B	Class 0 protostar	...	...	287±36	259±34	...	13
OMC-3 MMS6	Class 0 protostar	...	...	366±86	460±65	...	13
L1262-YSO	Class I protostar	**453±247**	**>430**	...	...	...	3,3
			>430				3
Several	Massive starless cores	...	65-1100	...	...	330-400	15,15
			180-1034$^{\#}$				15
Orion-KL Hot Core	Massive protostar	$170\pm^{140}_{80}$	...	...	...	...	16
Several	Massive protostars	...	190-1000	...	...	190-450	15,15
			180-1300				15
Several	Ultracompact HII regions	...	320-900	...	...	230-430	15,15
			350-700				15
Comets	JFC & Oort Cloud	$127^{\ddagger}$	...	139±26	...	$135\text{-}170^{\dagger}$	11,12,8

References: (1) Bizzocchi et al. (2013); (2) Hily-Blant et al. (2013a); (3) Milam & Charnley (2012), Adande et al. (2016); (4) Gerin et al. (2009); (5) Ikeda et al. (2002); (6) Lis et al. (2010); (7) Tennekes et al. (2006); (8) Hutsemékers et al. (2008); (9) Hily-Blant et al. (2013b); (10) Daniel et al. (2013), lower limit is for the $^{15}NNH^+$ isotopologue ; (11) Rousselot et al. (2014); (12) Bockelée-Morvan et al. (2008); (13) Wampfler et al. (2014); (15) Fontani et al. (2015) ; (16) Hermsen et al. (1986)

§ In each N_2H^+ entry the uppermost value is for the $^{15}NNH^+$ isotopologue. $^{\#}$ Larger value is a lower limit. † This range can be taken as a surrogate for the HCN ratio, however in comets there may be additional sources of CN (see Mumma & Charnley 2011). Only 2 measurements have been made for in HCN itself, in OC comets Hale-Bopp and 17P/Holmes. ‡ 'Average' based on optical observations of NH_3 daughter molecule NH_2 in an ensemble of comets.

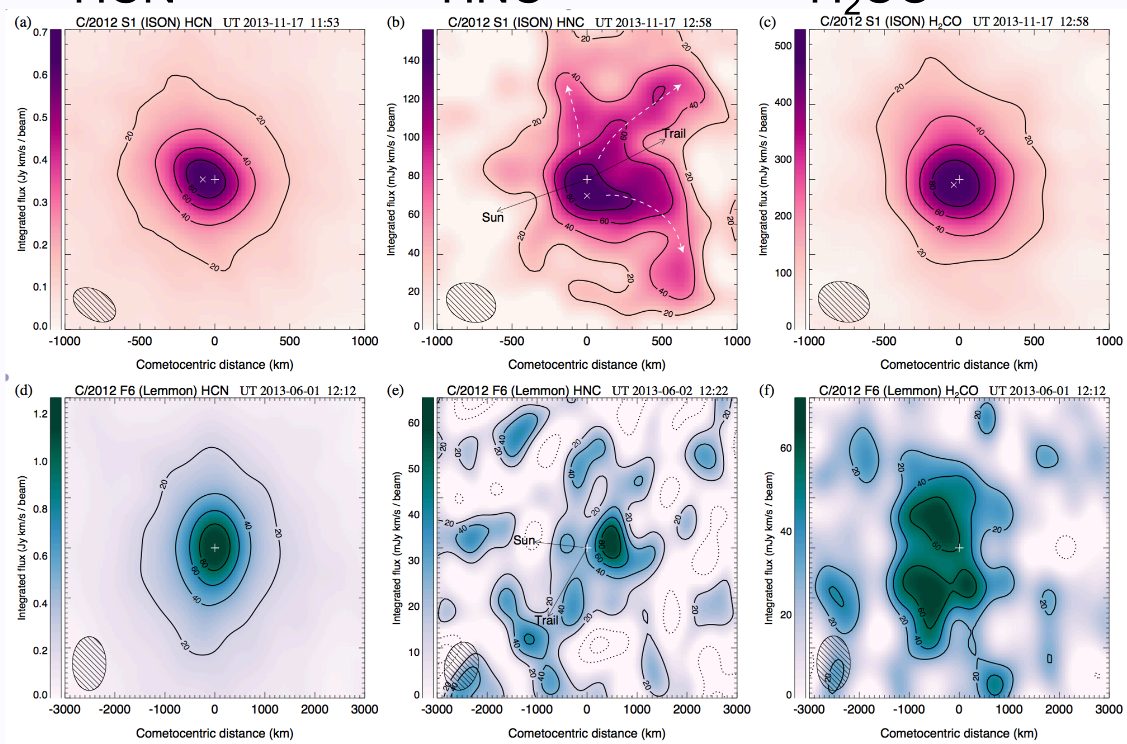
Adapted from Wirstroem et al. (2016)

HCN, HNC and CN in comets

HCN HNC H_2CO

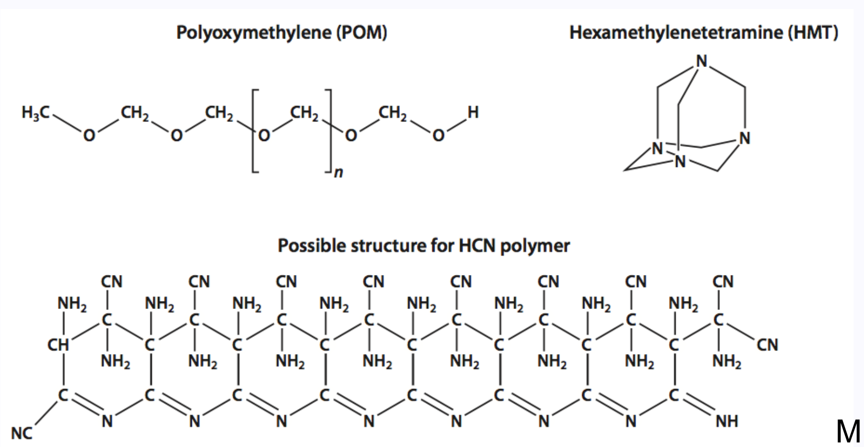
ISON

Lemmon



Modelling of data indicates extended sources of HNC and H_2CO ~ 300-2000 km from the nucleus

Cordiner et al. (2014)

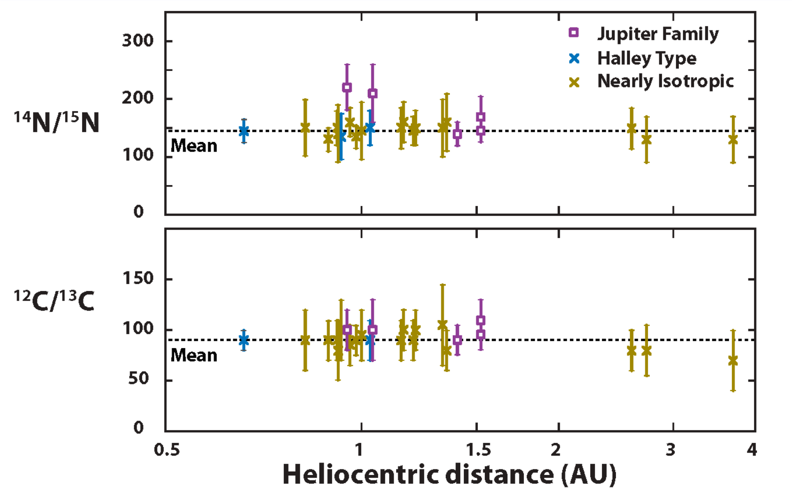


HNC has an unidentified parent such as HCN polymer, HMT or other macro-molecule, undergoing thermal or photo-degradation?

Similarly, not all cometary CN is a photoproduct of HCN (see also Hily-Blant et al. 2017 for TW Hya disk)

Mumma & Charnley 2011

$H^{13}CN$ & ^{13}CN in comets



$^{12}C^{14}N/^{12}C^{15}N$ ~ 120-150

$^{12}C^{14}N/^{13}C^{14}N$ ~ 90 ~ Solar

Cometary $H^{12}C^{14}N/H^{12}C^{15}N$ ~ 120-150

$H^{13}CN$ only detected in 3 comets (2 with Q~ 10^{31} s^{-1}) :

$H^{12}C^{14}N/H^{13}C^{14}N$ ~ 111 … Hale-Bopp

~ 114 … 17P/Holmes

Bockelee-Morvan et al. (2015)

~ 109 … Q2/Lovejoy

(Biver et al. 2016)

Summary

- $^{14}N/^{15}N$ traces Solar System origins: ISM-comets-meteorites
- Theoretical mechanism for fractionation of ISM molecules is uncertain
- Observations can provide insight into possible fractionation processes

ISSUES

- N_2 (N_2H^+) : Not known in primitive matter & comets. What causes the large $^{14}N/^{15}N$ spread ~150-1600 in ISM? $^{15}N_2H^+$ important ?
- $NH_3/^{15}NH_3$ ~ 130 in comets but ~300-600 in ISM. Why?
- HCN/HC^{15}N : similar ratios in ISM, comets & disks (Guzman et al. 2017) but now showing a large spread in ISM (Zeng et al. 2017; Colzi et al. 2017)
- HNC/H^{15}NC : less enriched than HCN in regions of massive SF
- CN/C^{15}N : ~120-300 in comets; ~190-450 in ISM; ~323 in a disk (Hily-Blant et al. 2017)
- ISM: HCN, HNC & CN difficult to understand if $HCNH^+$ involved
- Comets: 2 differently fractionated reservoirs for HCN and HNC+CN possible …
- Primitive matter: nature of the ^{15}N carrier ?

END