A Connection Between Interstellar and Solar System Isotopic Fractionation?

Steven Charnley

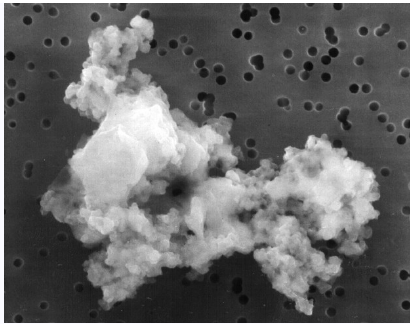
NASA Goddard Space Flight Center

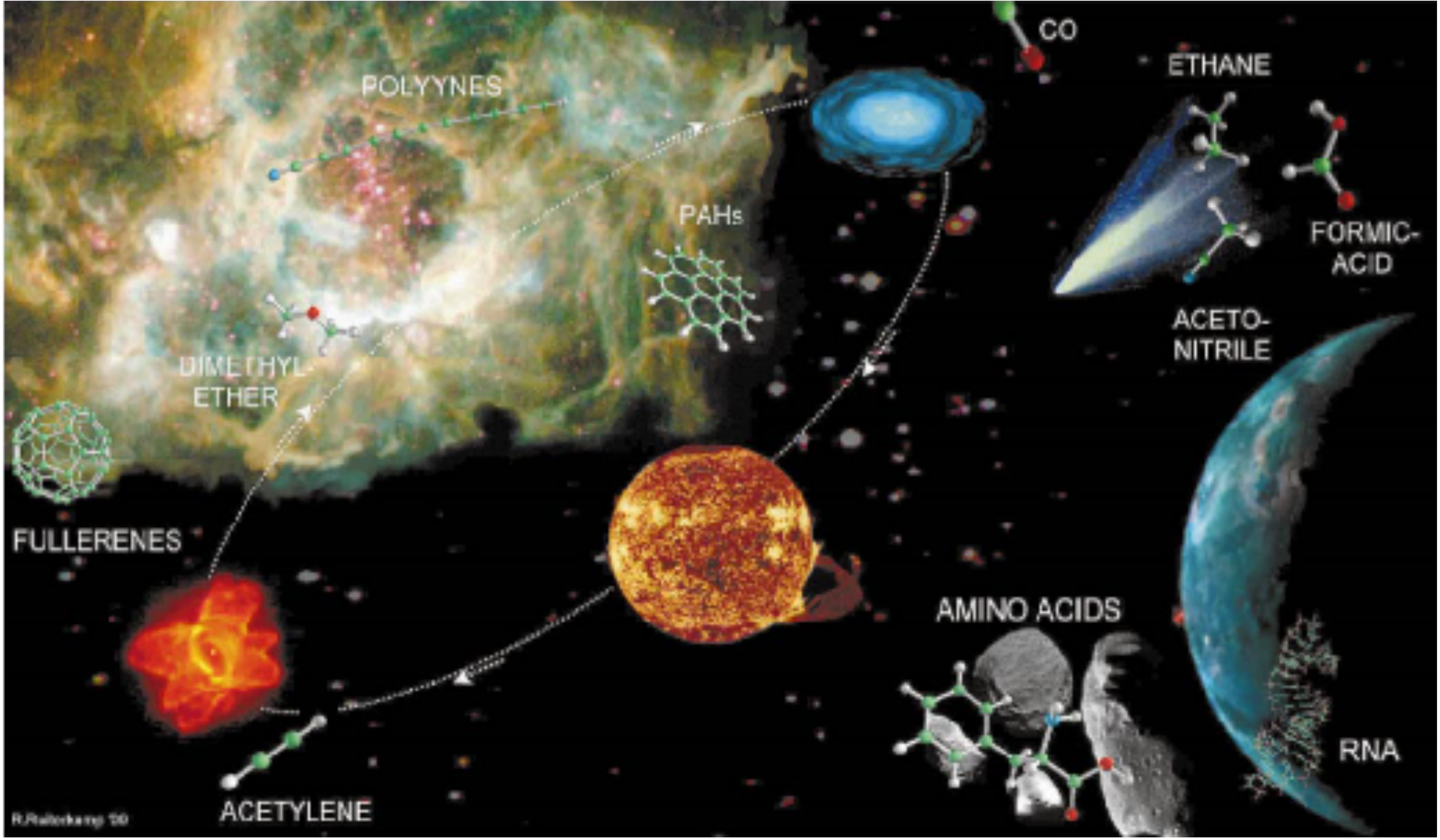
Fractionation of isotopes in space: from the solar system to galaxies
Arcetri Observatory
October 12 2016

ISM-Solar System Isotopic Connection?

Primitive material = comets, asteroids, meteorites, IDPs

Isotopic fractionation a remnant of cold interstellar chemistry ?

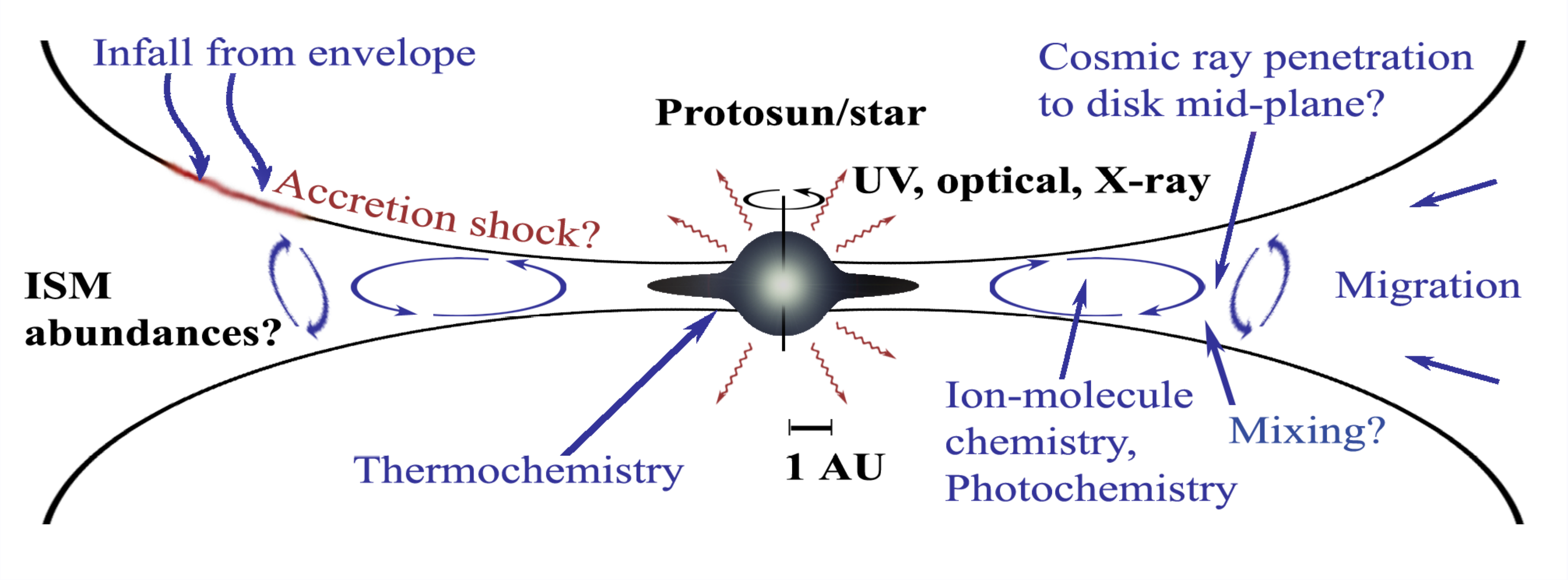




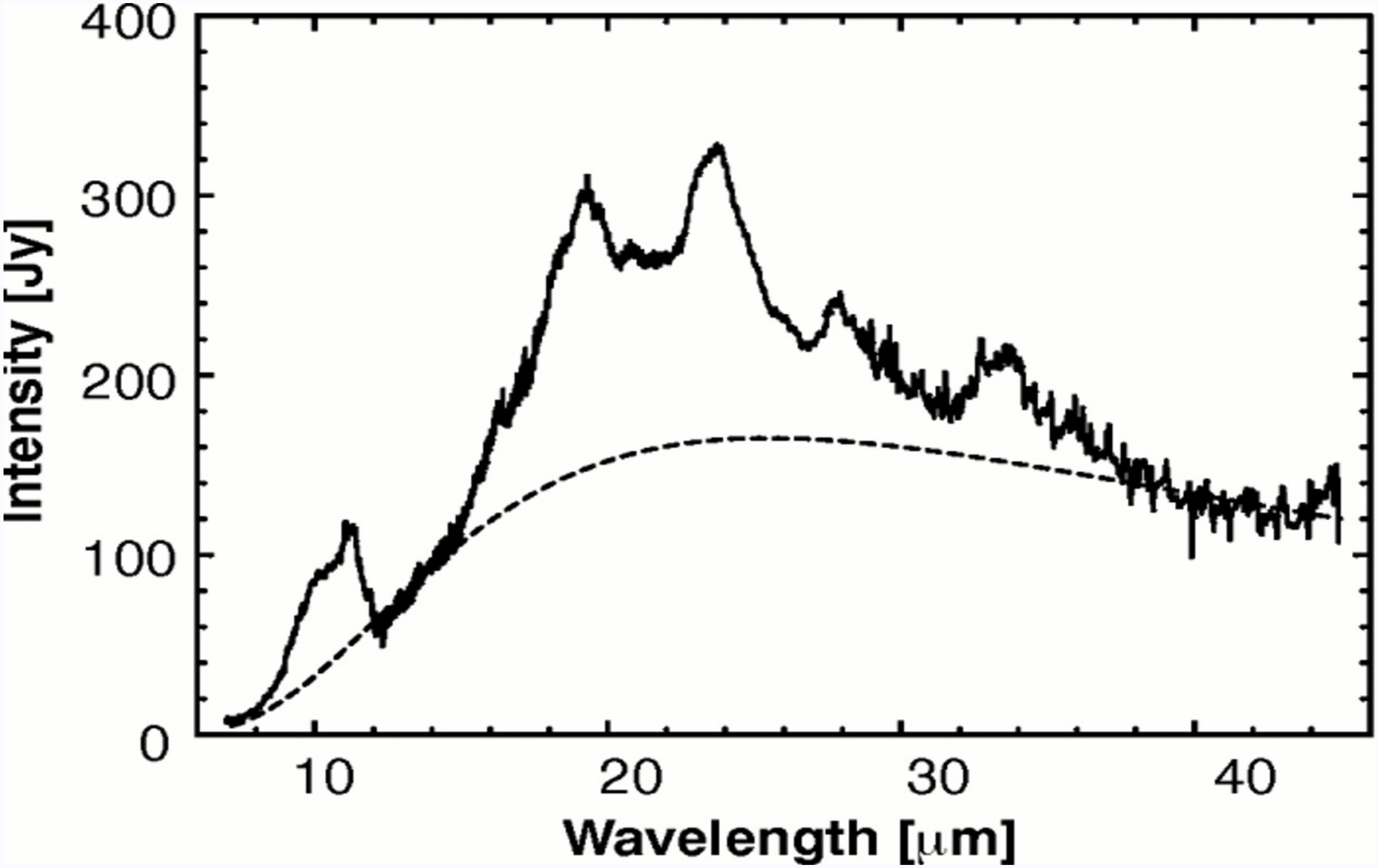
OVERVIEW

- **Isotopic evidence for a comet-ISM connection**
- **Interstellar chemistry in comets**
- **Interstellar precursors of meteoritic organics**

Interstellar ices and dust in protoplanetary disks

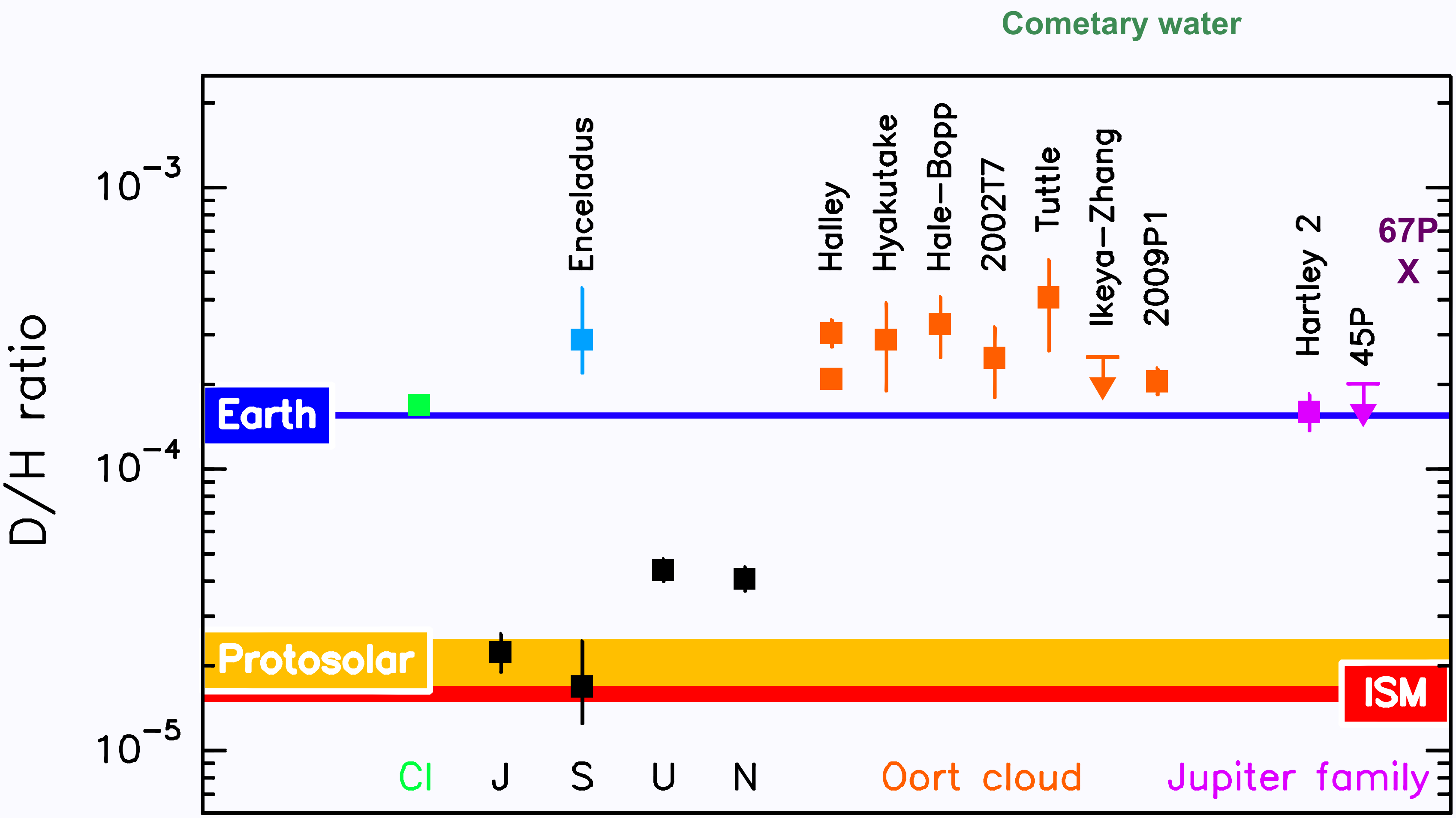


Comet Dust



Crovisier et al. (1997)

D/H IN THE SOLAR SYSTEM



Adapted from Bockelee-Morvan et al. (2015)

D/H: COMETS vs. ISM

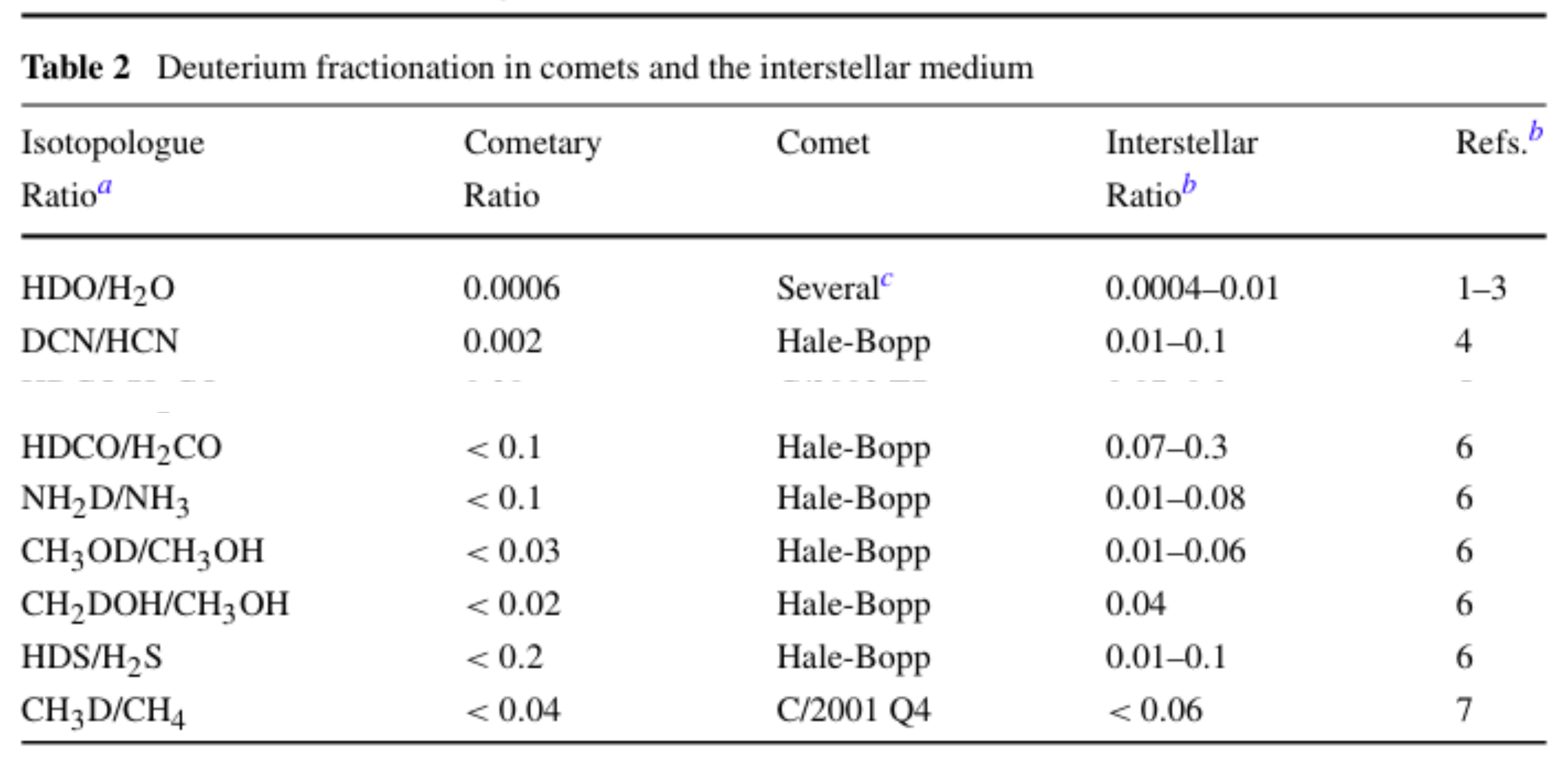


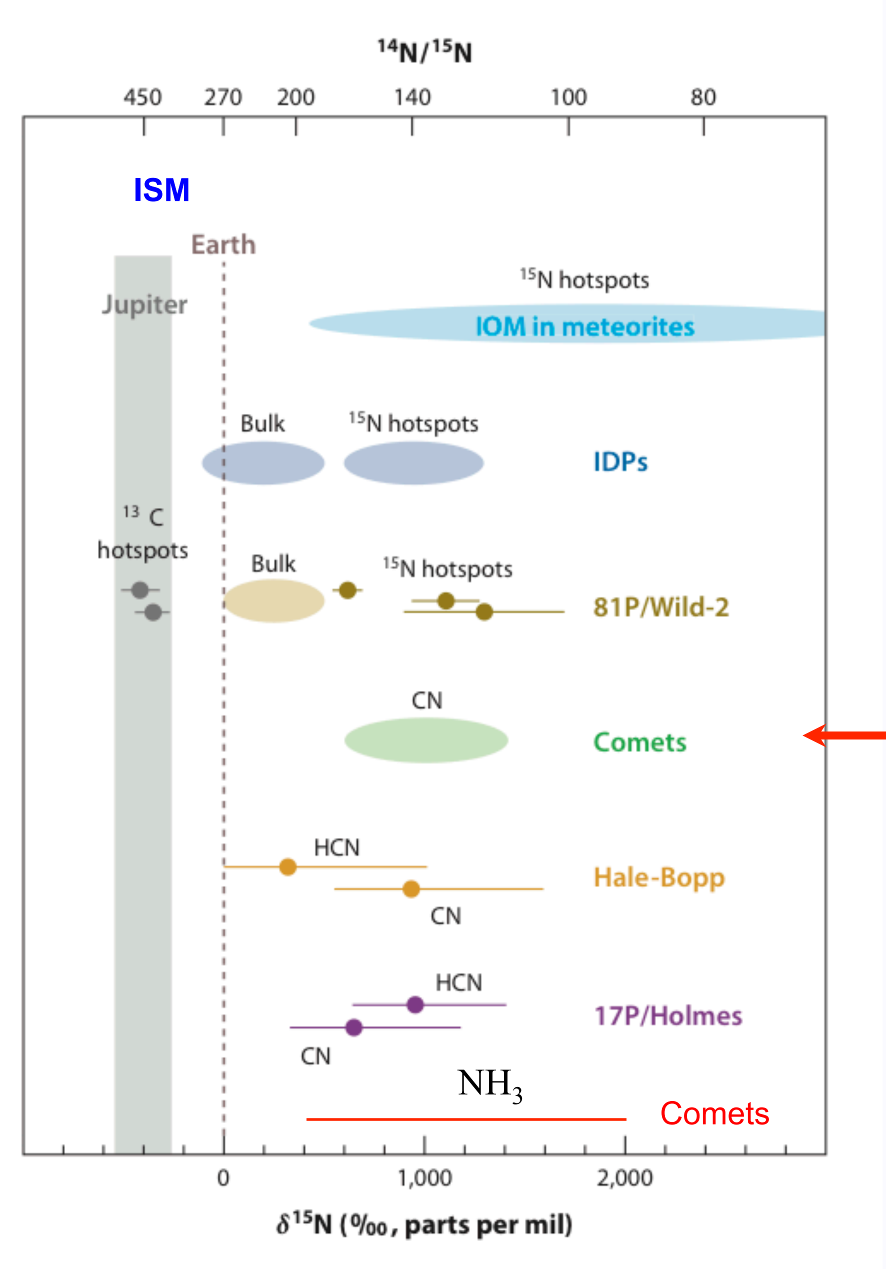
Table 2 Deuterium fractionation in comets and the interstellar medium

Isotopologue Ratio[a]	Cometary Ratio	Comet	Interstellar Ratio[b]	Refs.[b]
HDO/H_2O	0.0006	Several[c]	0.0004–0.01	1–3
DCN/HCN	0.002	Hale-Bopp	0.01–0.1	4
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
$HDCO/H_2CO$	< 0.1	Hale-Bopp	0.07–0.3	6
NH_2D/NH_3	< 0.1	Hale-Bopp	0.01–0.08	6
CH_3OD/CH_3OH	< 0.03	Hale-Bopp	0.01–0.06	6
CH_2DOH/CH_3OH	< 0.02	Hale-Bopp	0.04	6
HDS/H_2S	< 0.2	Hale-Bopp	0.01–0.1	6
CH_3D/CH_4	< 0.04	C/2001 Q4	< 0.06	7

Charnley & Rodgers (2008)

See also Bockelee-Morvan et al. (2015)

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

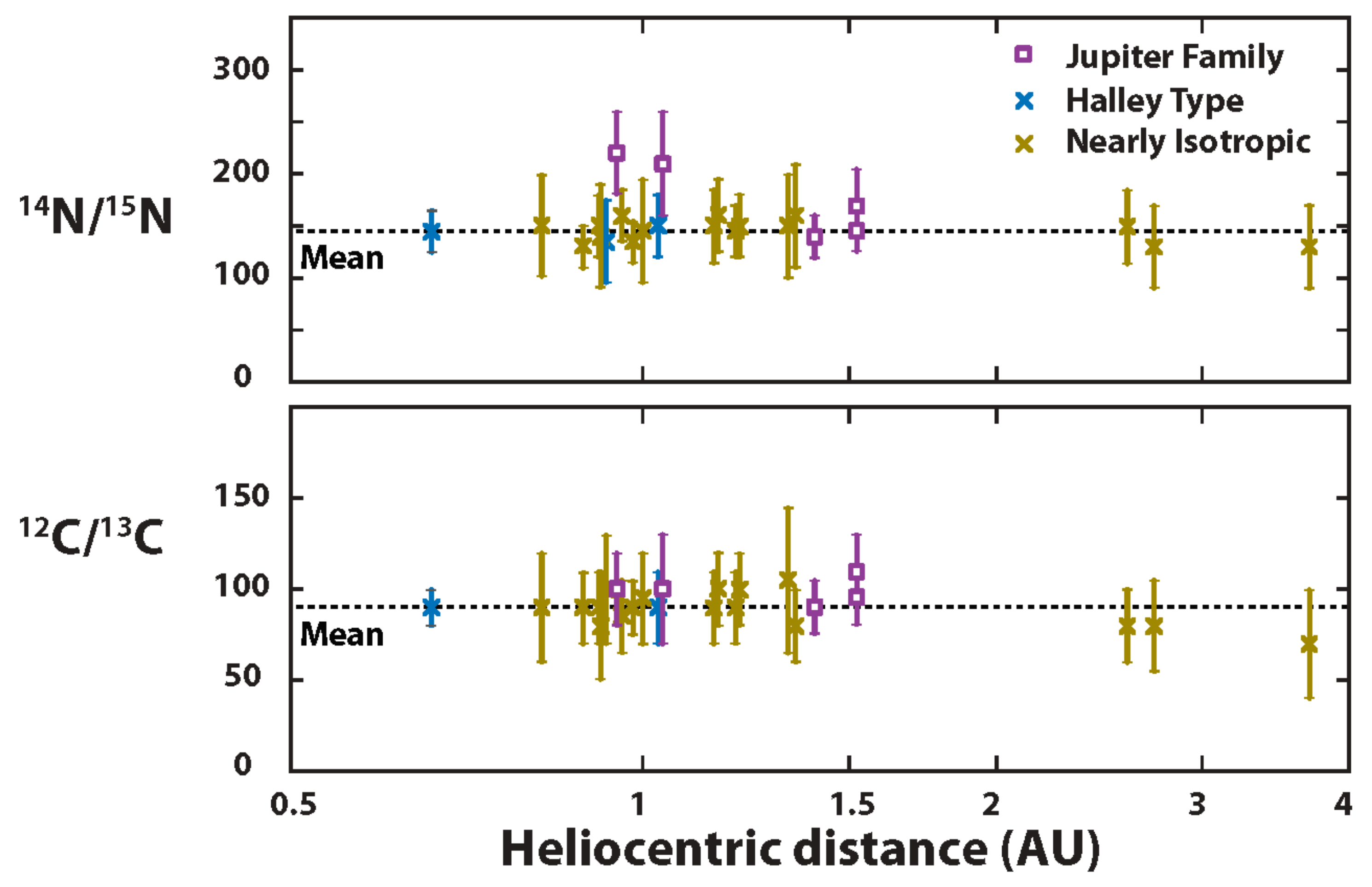


Measured in > 20 comets

Adapted from Mumma & Charnley (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?

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)

$$
\begin{aligned}
{}^{15}N + {}^{14}N_2H^+ &\rightleftharpoons {}^{14}N + {}^{15}N^{14}NH^+ \\
&\rightleftharpoons {}^{14}N + {}^{14}N^{15}NH^+
\end{aligned}
$$

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

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

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

Terzieva & Herbst (2000)

$$
\begin{aligned}
H_3^+ + HD &\rightleftharpoons H_2D^+ + H_2 \\
H_2D^+ + HD &\rightleftharpoons D_2H^+ + H_2 \\
D_2H^+ + HD &\rightleftharpoons D_3^+ + H_2
\end{aligned}
$$

Roberts et al. (2003)

^{15}N Fractionation in Meteorites

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

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

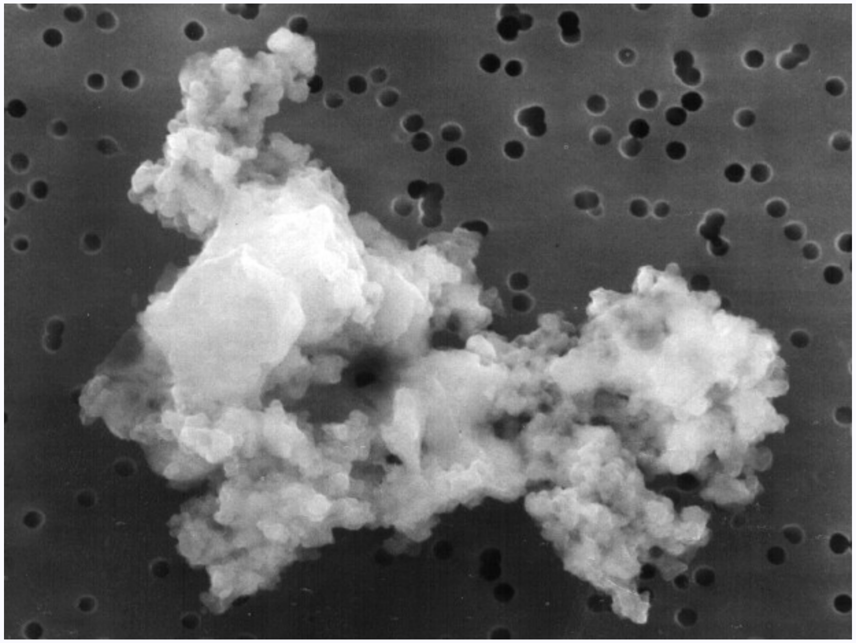
Meteorites & IDPs:

`hotspots':

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

D-rich + ^{15}N-poor

^{15}N-rich + D-poor

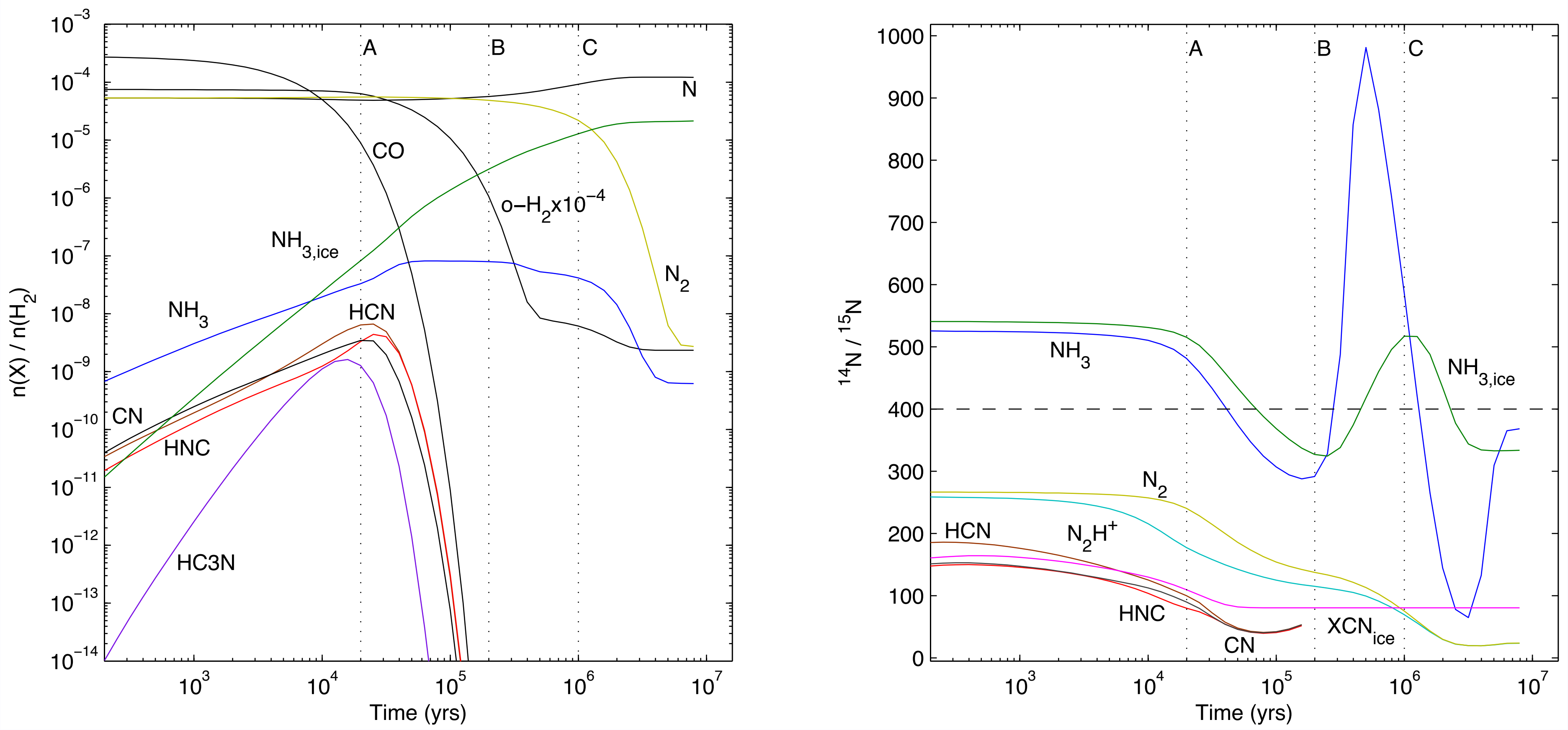


Present in the Insoluble and Soluble Organic Material

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

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)

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

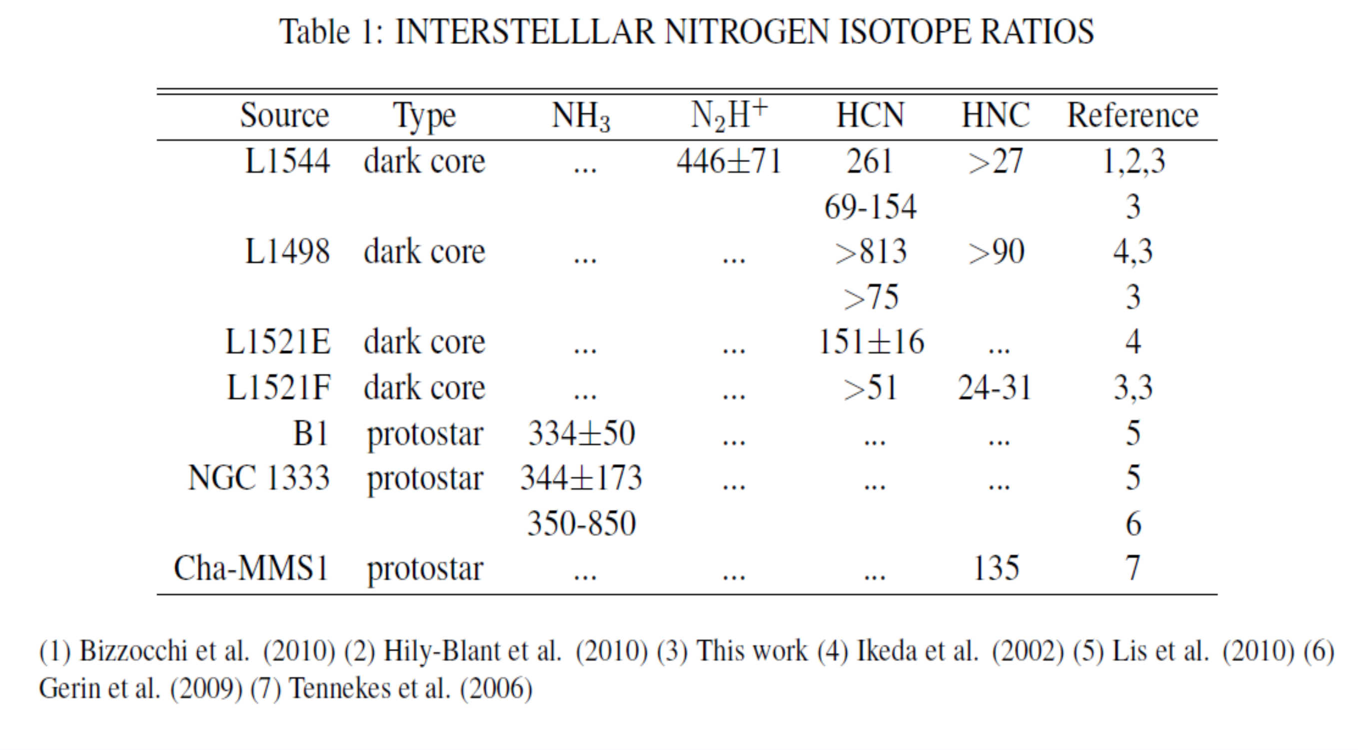


Table 1: INTERSTELLLAR NITROGEN ISOTOPE RATIOS

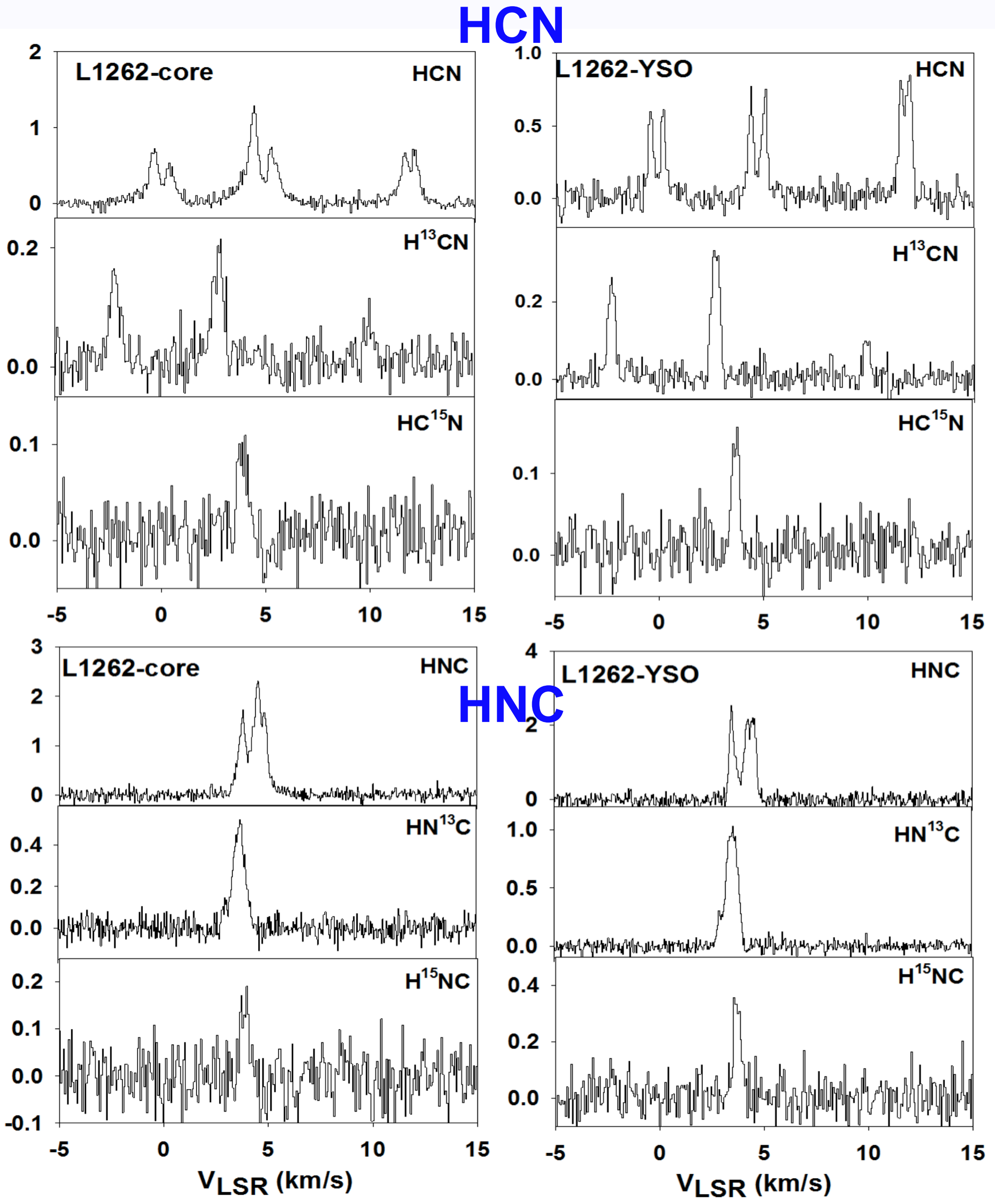
Source	Type	NH_3	N_2H^+	HCN	HNC	Reference
L1544	dark core	...	446±71	261	>27	1,2,3
				69-154		3
L1498	dark core	...	...	>813	>90	4,3
				>75		3
L1521E	dark core	...	...	151±16	...	4
L1521F	dark core	...	...	>51	24-31	3,3
B1	protostar	334±50	...	...	...	5
NGC 1333	protostar	344±173	...	...	...	5
		350-850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

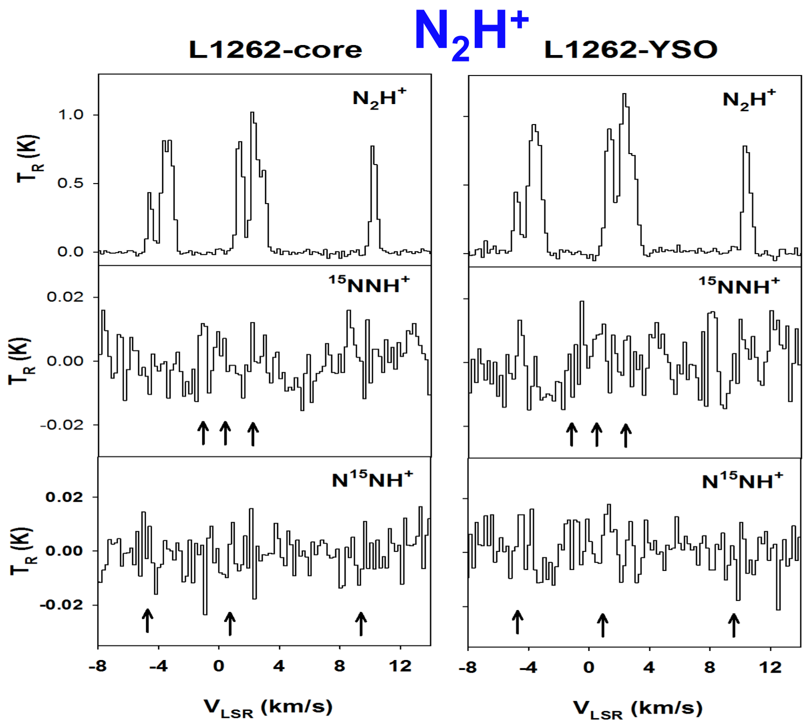
(1) Bizzocchi et al. (2010) (2) Hily-Blant et al. (2010) (3) This work (4) Ikeda et al. (2002) (5) Lis et al. (2010) (6) Gerin et al. (2009) (7) Tennekes et al. (2006)

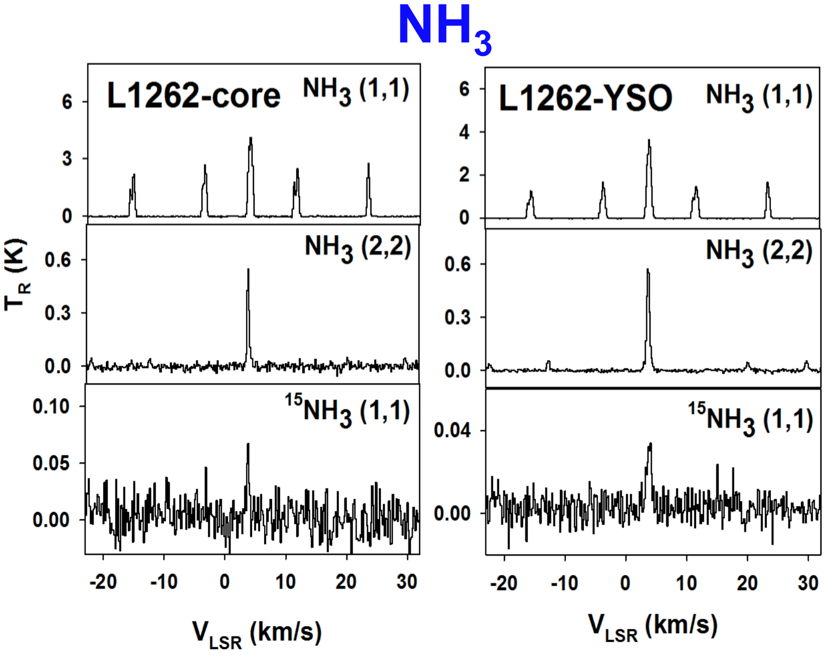
Milam & Charnley (2010)

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

Adande et al. (2016a & b)







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	...	135-170†	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. (2015)

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

- $^{14}N/^{15}N$ 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) now calculate barriers for the key processes:

$$\begin{aligned} ^{15}\mathrm{N} + {}^{14}\mathrm{N}_2\mathrm{H}^+ &\rightleftharpoons {}^{14}\mathrm{N} + {}^{15}\mathrm{N}^{14}\mathrm{NH}^+ \\ &\rightleftharpoons {}^{14}\mathrm{N} + {}^{14}\mathrm{N}^{15}\mathrm{NH}^+ \end{aligned}$$

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

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

- Models need to be re-evaluated (Wirstroem & Charnley 2016)

Interstellar and Cometary Ices

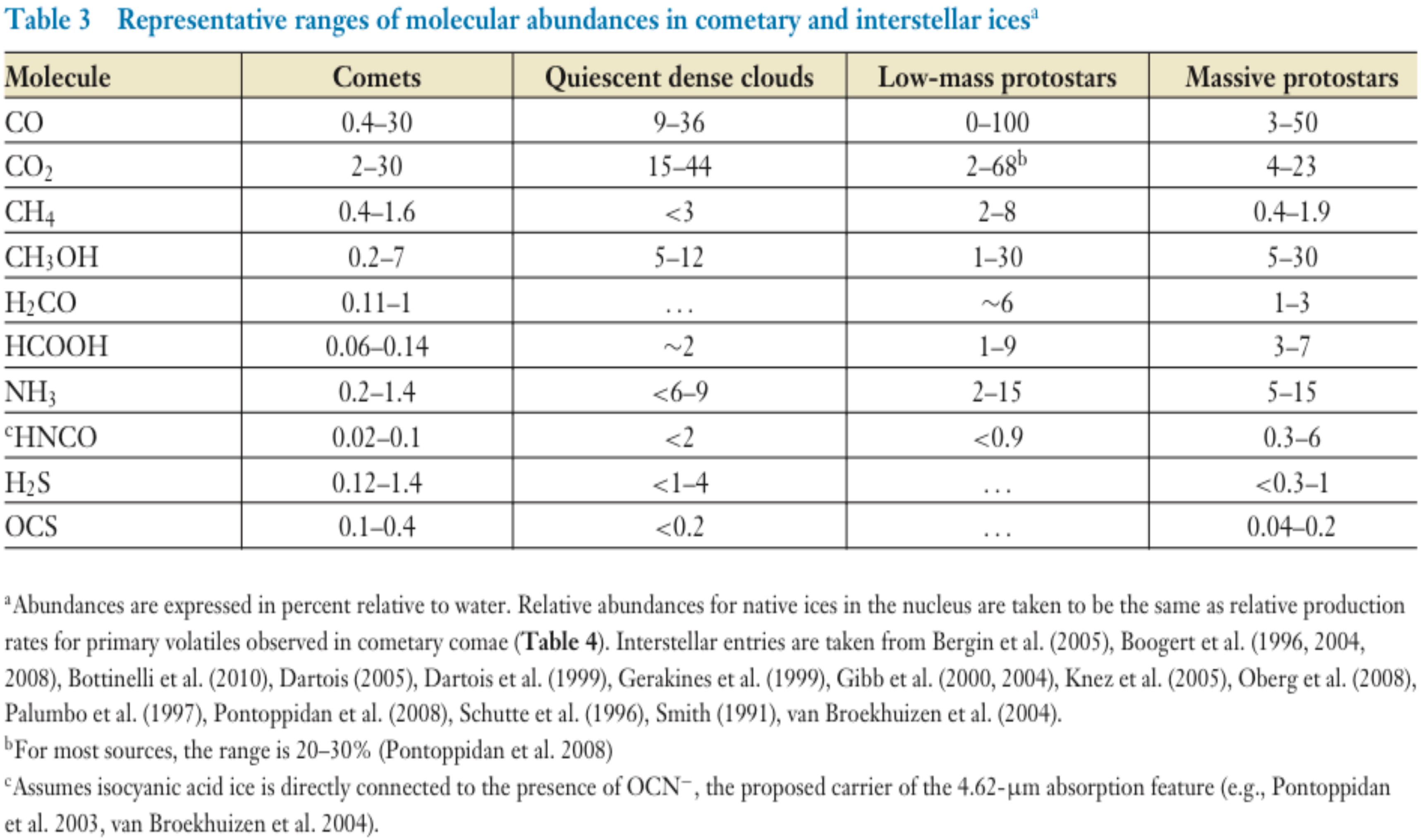


Table 3 Representative ranges of molecular abundances in cometary and interstellar ices[a]

Molecule	Comets	Quiescent dense clouds	Low-mass protostars	Massive protostars
CO	0.4–30	9–36	0–100	3–50
CO_2	2–30	15–44	2–68[b]	4–23
CH_4	0.4–1.6	<3	2–8	0.4–1.9
CH_3OH	0.2–7	5–12	1–30	5–30
H_2CO	0.11–1	. . .	~6	1–3
HCOOH	0.06–0.14	~2	1–9	3–7
NH_3	0.2–1.4	<6–9	2–15	5–15
[c]HNCO	0.02–0.1	<2	<0.9	0.3–6
H_2S	0.12–1.4	<1–4	. . .	<0.3–1
OCS	0.1–0.4	<0.2	. . .	0.04–0.2

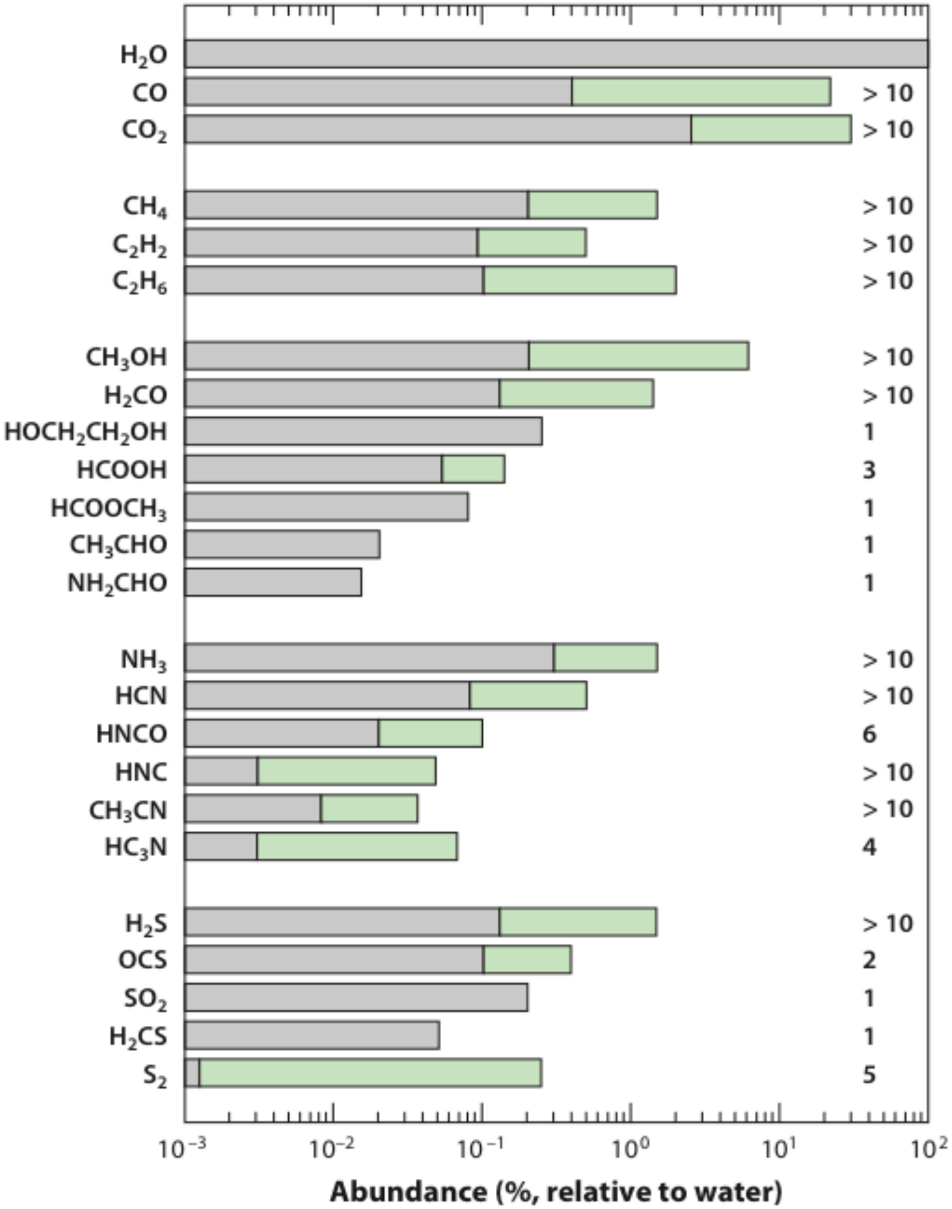
[a] Abundances are expressed in percent relative to water. Relative abundances for native ices in the nucleus are taken to be the same as relative production rates for primary volatiles observed in cometary comae (**Table 4**). Interstellar entries are taken from Bergin et al. (2005), Boogert et al. (1996, 2004, 2008), Bottinelli et al. (2010), Dartois (2005), Dartois et al. (1999), Gerakines et al. (1999), Gibb et al. (2000, 2004), Knez et al. (2005), Oberg et al. (2008), Palumbo et al. (1997), Pontoppidan et al. (2008), Schutte et al. (1996), Smith (1991), van Broekhuizen et al. (2004).

[b] For most sources, the range is 20–30% (Pontoppidan et al. 2008)

[c] Assumes isocyanic acid ice is directly connected to the presence of OCN^-, the proposed carrier of the 4.62-μm absorption feature (e.g., Pontoppidan et al. 2003, van Broekhuizen et al. 2004).

From Mumma & Charnley 2011

Molecules in the Coma



Mumma & Charnley 2011

Recent observations indicate that

$(CH_2OH)_2$, NH_2CHO,
HNCO, CH_3CHO, HCOOH,
CH_2OHCHO, CH_3CH_2OH
are probably common in comets.

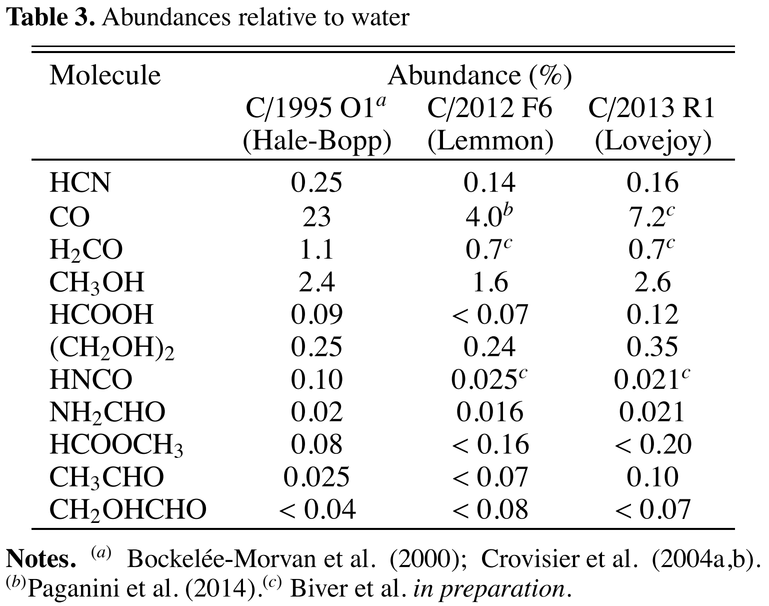


Table 3. Abundances relative to water

Molecule	Abundance (%)		
	C/1995 O1[a] (Hale-Bopp)	C/2012 F6 (Lemmon)	C/2013 R1 (Lovejoy)
HCN	0.25	0.14	0.16
CO	23	4.0[b]	7.2[c]
H_2CO	1.1	0.7[c]	0.7[c]
CH_3OH	2.4	1.6	2.6
HCOOH	0.09	< 0.07	0.12
$(CH_2OH)_2$	0.25	0.24	0.35
HNCO	0.10	0.025[c]	0.021[c]
NH_2CHO	0.02	0.016	0.021
$HCOOCH_3$	0.08	< 0.16	< 0.20
CH_3CHO	0.025	< 0.07	0.10
CH_2OHCHO	< 0.04	< 0.08	< 0.07

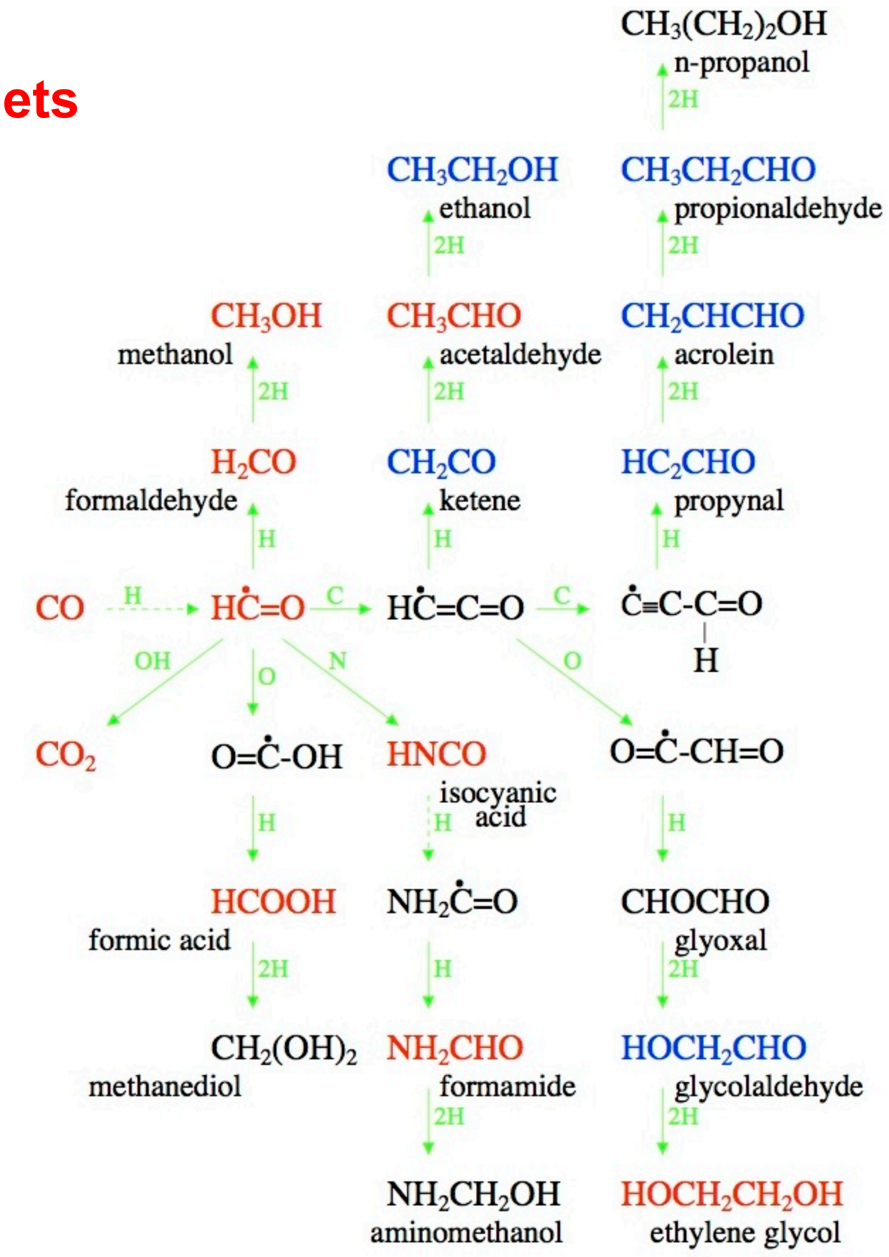
Notes. (a) Bockelée-Morvan et al. (2000); Crovisier et al. (2004a,b). (b) Paganini et al. (2014). (c) Biver et al. *in preparation*.

Biver et al. (2014, 2015)

Atom Addition Reactions on Cold Dust

Both ISM & comets

ISM only

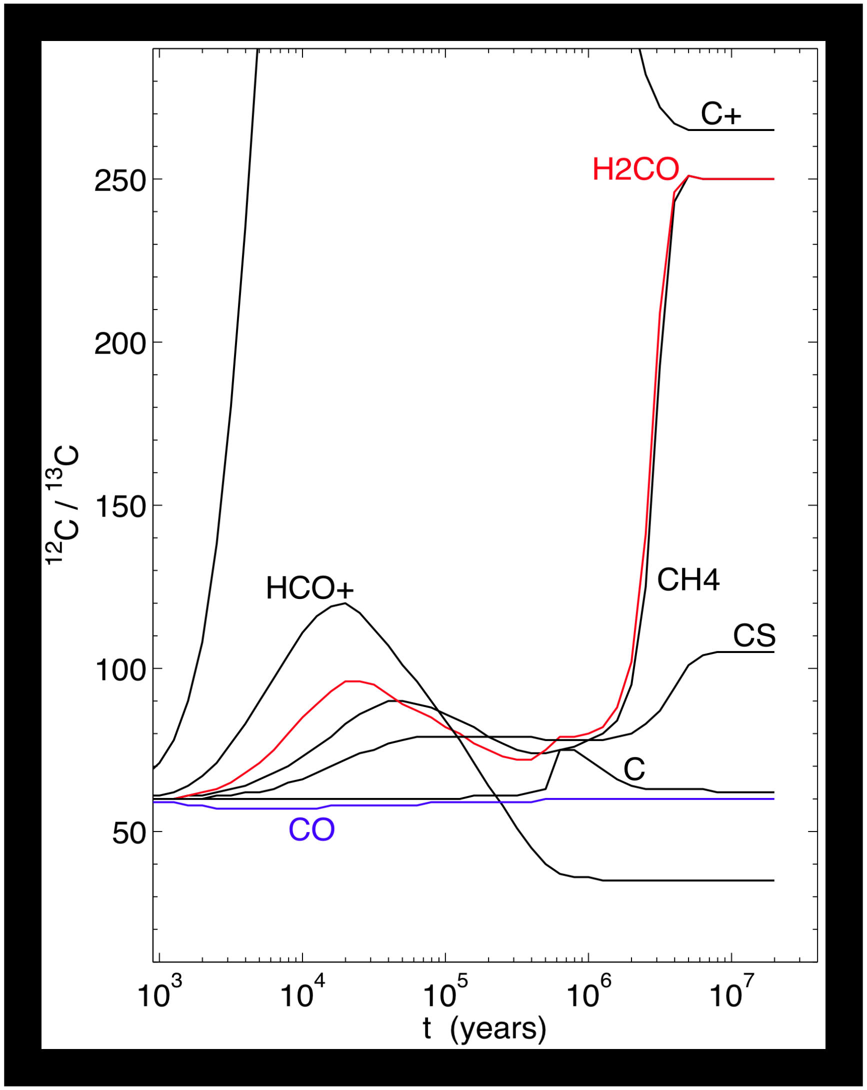


Charnley & Rodgers (2008)

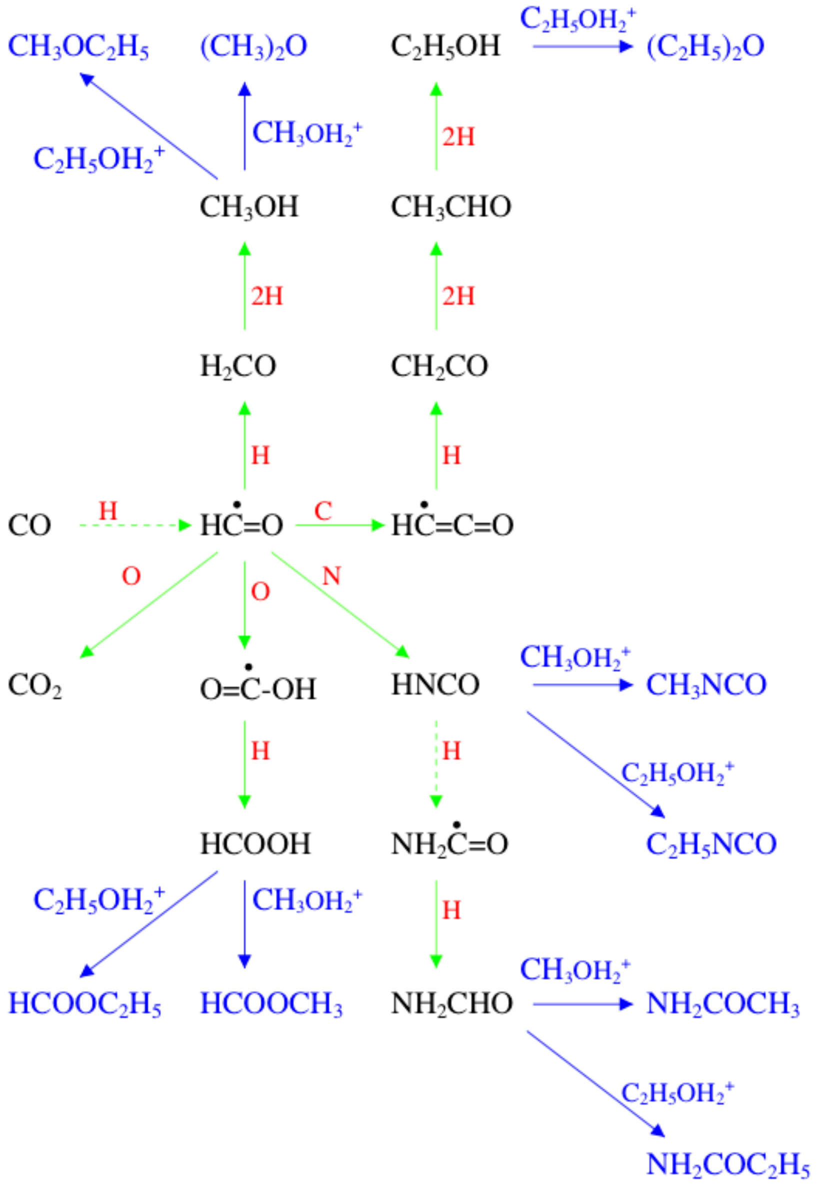
Isotopes: ^{13}C Labelling

Cold gas: $^{13}C^+ + {}^{12}CO \longrightarrow {}^{12}C^+ + {}^{13}CO$

Langer et al. (1984)



Dust formation and post-evaporation gas formation



$CH_3OC_2H_5$ $(CH_3)_2O$ C_2H_5OH $\xrightarrow{C_2H_5OH_2^+}$ $(C_2H_5)_2O$

$C_2H_5OH_2^+$ $CH_3OH_2^+$ 2H

CH_3OH CH_3CHO

2H 2H

H_2CO CH_2CO

H H

CO $\xrightarrow{H}$ $H\dot{C}{=}O$ $\xrightarrow{C}$ $H\dot{C}{=}C{=}O$

O O N

CO_2 $O{=}\dot{C}{-}OH$ HNCO $\xrightarrow{CH_3OH_2^+}$ CH_3NCO

H H $C_2H_5OH_2^+$

HCOOH $NH_2\dot{C}{=}O$ C_2H_5NCO

$C_2H_5OH_2^+$ $CH_3OH_2^+$ H

$HCOOC_2H_5$ $HCOOCH_3$ NH_2CHO $\xrightarrow{CH_3OH_2^+}$ NH_2COCH_3

$C_2H_5OH_2^+$

$NH_2COC_2H_5$

Posterior Isotopic Labelling

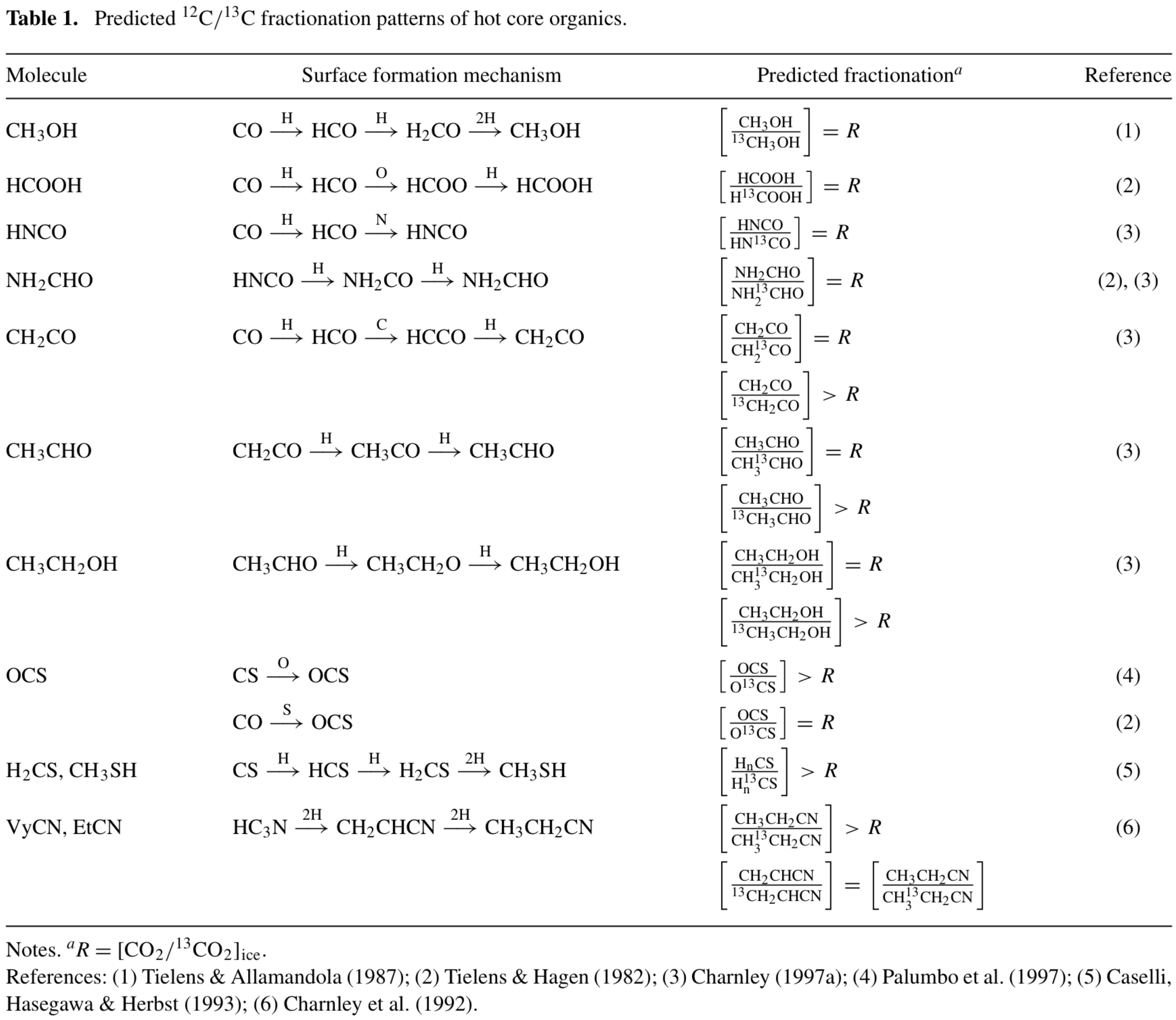


Table 1. Predicted $^{12}\mathrm{C}/^{13}\mathrm{C}$ fractionation patterns of hot core organics.

Molecule	Surface formation mechanism	Predicted fractionation[a]	Reference
$\mathrm{CH_3OH}$	$\mathrm{CO} \xrightarrow{\mathrm{H}} \mathrm{HCO} \xrightarrow{\mathrm{H}} \mathrm{H_2CO} \xrightarrow{\mathrm{2H}} \mathrm{CH_3OH}$	$\left[\frac{\mathrm{CH_3OH}}{\mathrm{^{13}CH_3OH}}\right] = R$	(1)
HCOOH	$\mathrm{CO} \xrightarrow{\mathrm{H}} \mathrm{HCO} \xrightarrow{\mathrm{O}} \mathrm{HCOO} \xrightarrow{\mathrm{H}} \mathrm{HCOOH}$	$\left[\frac{\mathrm{HCOOH}}{\mathrm{H^{13}COOH}}\right] = R$	(2)
HNCO	$\mathrm{CO} \xrightarrow{\mathrm{H}} \mathrm{HCO} \xrightarrow{\mathrm{N}} \mathrm{HNCO}$	$\left[\frac{\mathrm{HNCO}}{\mathrm{HN^{13}CO}}\right] = R$	(3)
$\mathrm{NH_2CHO}$	$\mathrm{HNCO} \xrightarrow{\mathrm{H}} \mathrm{NH_2CO} \xrightarrow{\mathrm{H}} \mathrm{NH_2CHO}$	$\left[\frac{\mathrm{NH_2CHO}}{\mathrm{NH_2^{13}CHO}}\right] = R$	(2), (3)
$\mathrm{CH_2CO}$	$\mathrm{CO} \xrightarrow{\mathrm{H}} \mathrm{HCO} \xrightarrow{\mathrm{C}} \mathrm{HCCO} \xrightarrow{\mathrm{H}} \mathrm{CH_2CO}$	$\left[\frac{\mathrm{CH_2CO}}{\mathrm{CH_2^{13}CO}}\right] = R$	(3)
		$\left[\frac{\mathrm{CH_2CO}}{\mathrm{^{13}CH_2CO}}\right] > R$	
$\mathrm{CH_3CHO}$	$\mathrm{CH_2CO} \xrightarrow{\mathrm{H}} \mathrm{CH_3CO} \xrightarrow{\mathrm{H}} \mathrm{CH_3CHO}$	$\left[\frac{\mathrm{CH_3CHO}}{\mathrm{CH_3^{13}CHO}}\right] = R$	(3)
		$\left[\frac{\mathrm{CH_3CHO}}{\mathrm{^{13}CH_3CHO}}\right] > R$	
$\mathrm{CH_3CH_2OH}$	$\mathrm{CH_3CHO} \xrightarrow{\mathrm{H}} \mathrm{CH_3CH_2O} \xrightarrow{\mathrm{H}} \mathrm{CH_3CH_2OH}$	$\left[\frac{\mathrm{CH_3CH_2OH}}{\mathrm{CH_3^{13}CH_2OH}}\right] = R$	(3)
		$\left[\frac{\mathrm{CH_3CH_2OH}}{\mathrm{^{13}CH_3CH_2OH}}\right] > R$	
OCS	$\mathrm{CS} \xrightarrow{\mathrm{O}} \mathrm{OCS}$	$\left[\frac{\mathrm{OCS}}{\mathrm{O^{13}CS}}\right] > R$	(4)
	$\mathrm{CO} \xrightarrow{\mathrm{S}} \mathrm{OCS}$	$\left[\frac{\mathrm{OCS}}{\mathrm{O^{13}CS}}\right] = R$	(2)
$\mathrm{H_2CS}$, $\mathrm{CH_3SH}$	$\mathrm{CS} \xrightarrow{\mathrm{H}} \mathrm{HCS} \xrightarrow{\mathrm{H}} \mathrm{H_2CS} \xrightarrow{\mathrm{2H}} \mathrm{CH_3SH}$	$\left[\frac{\mathrm{H_nCS}}{\mathrm{H_n^{13}CS}}\right] > R$	(5)
VyCN, EtCN	$\mathrm{HC_3N} \xrightarrow{\mathrm{2H}} \mathrm{CH_2CHCN} \xrightarrow{\mathrm{2H}} \mathrm{CH_3CH_2CN}$	$\left[\frac{\mathrm{CH_3CH_2CN}}{\mathrm{CH_3^{13}CH_2CN}}\right] > R$	(6)
		$\left[\frac{\mathrm{CH_2CHCN}}{\mathrm{^{13}CH_2CHCN}}\right] = \left[\frac{\mathrm{CH_3CH_2CN}}{\mathrm{CH_3^{13}CH_2CN}}\right]$	

Notes. [a] $R = [\mathrm{CO_2}/^{13}\mathrm{CO_2}]_{\mathrm{ice}}$.

References: (1) Tielens & Allamandola (1987); (2) Tielens & Hagen (1982); (3) Charnley (1997a); (4) Palumbo et al. (1997); (5) Caselli, Hasegawa & Herbst (1993); (6) Charnley et al. (1992).

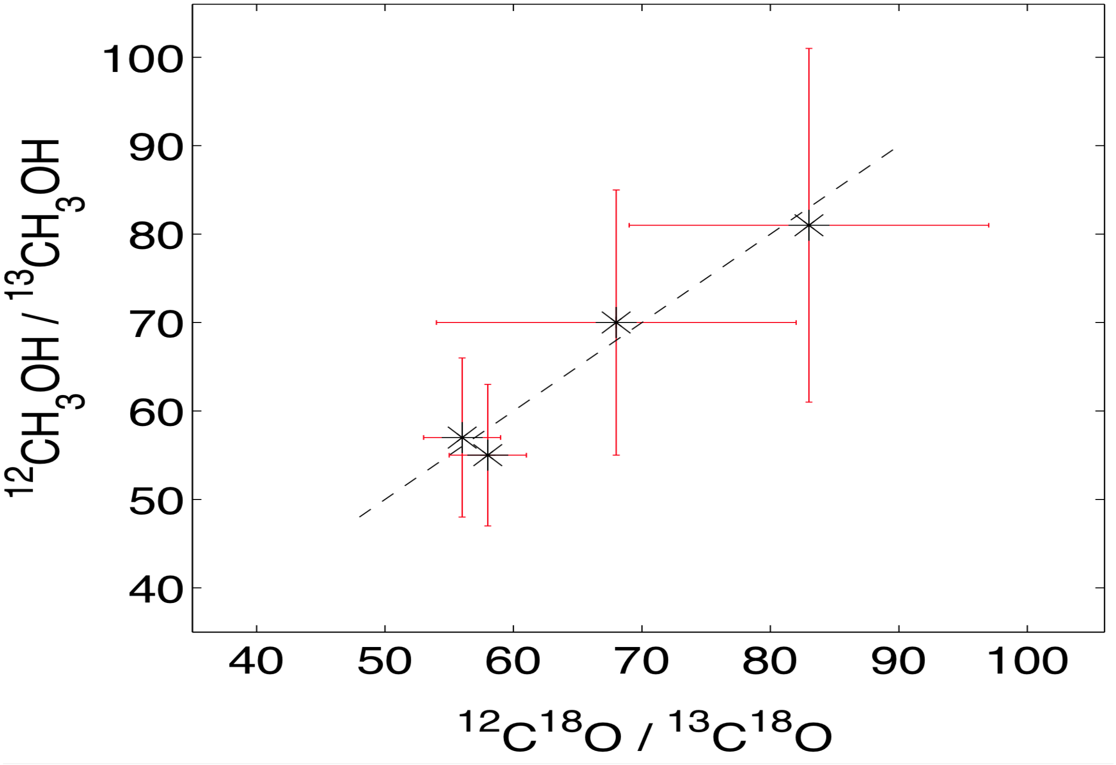
Charnley et al. (2004)

$^{12}C/^{13}C$ Observed in CO, CO_2, H_2CO and CH_3OH

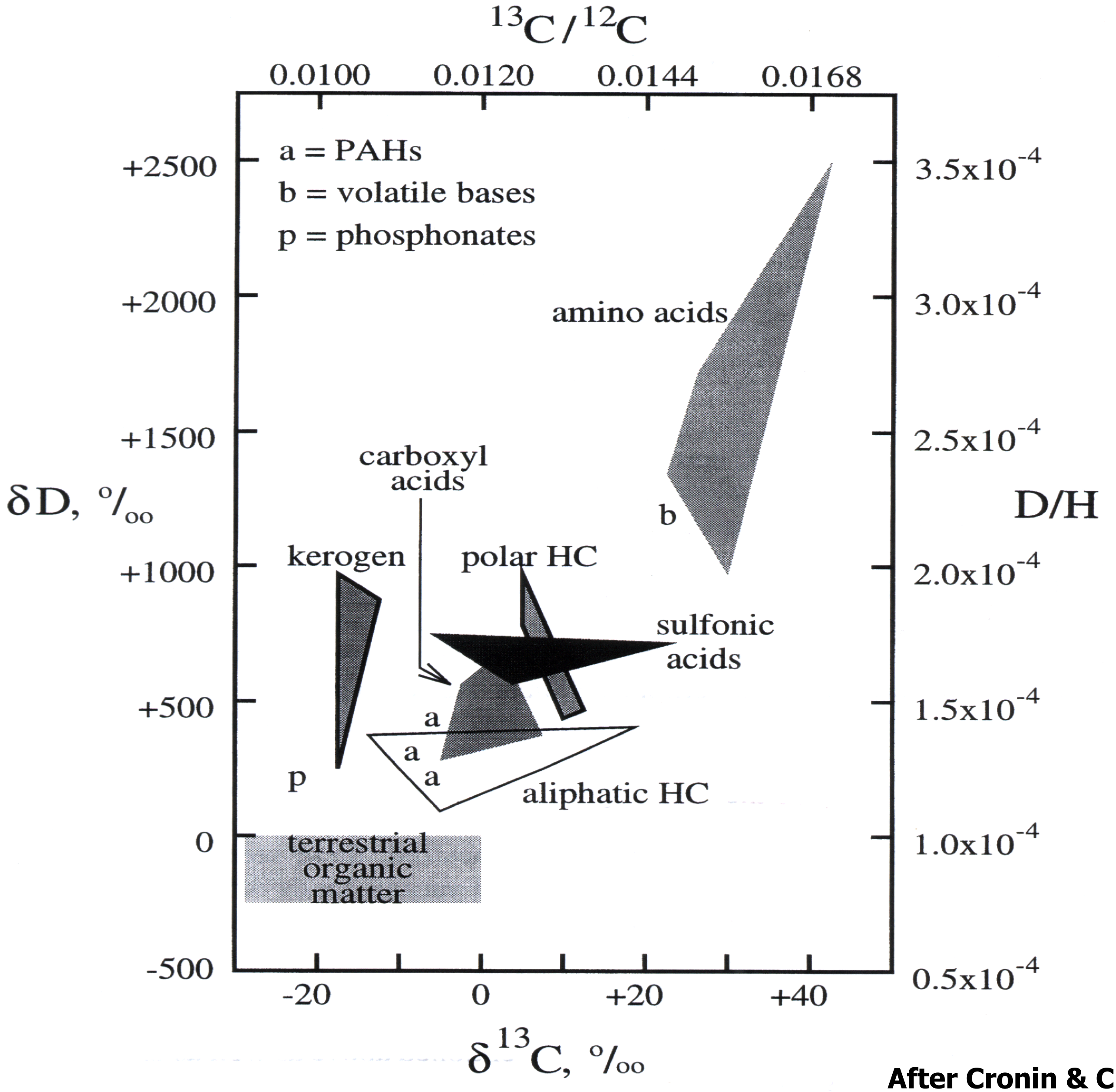
Boogert et al. (2000, 2002): CO & CO_2 ice with *ISO*

Wirstroem et al. (2011) CH_3OH
Wirstroem et al. (in prep.): H_2CO

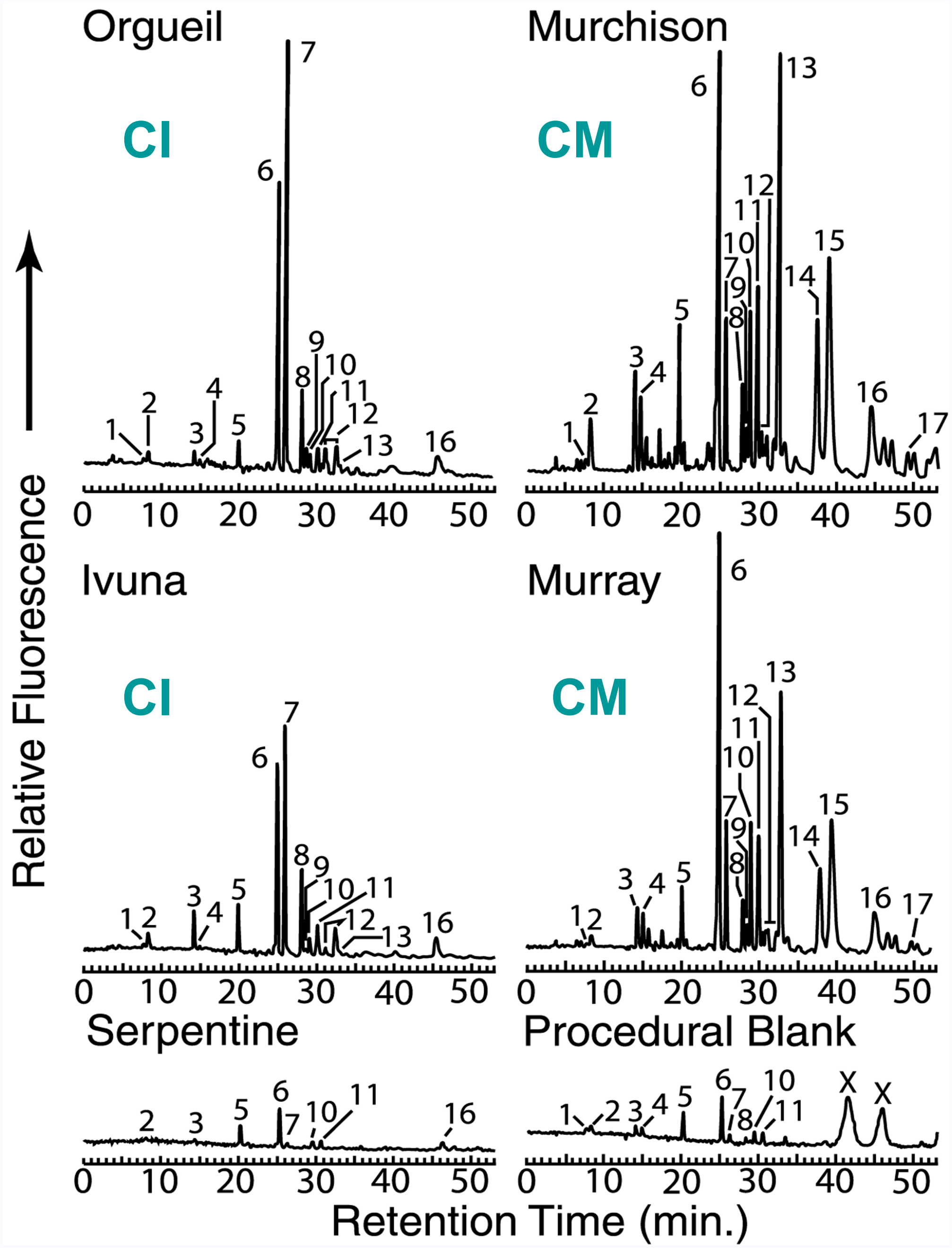
Measured in massive protostellar cores (Onsala, ARO):
AFGL 2591, NGC 7538 IRS1 &IRS9, S140 IRS1, NGC 2264 IRS1,
DR 21(OH), W51 e1/e2



D and C isotopic fractionation in the Murchison meteorite



After Cronin & Chang (1993)



Amino Acids in Meteorite Extracts

1	D-Aspartic Acid
2	L-Aspartic Acid
3	L-Glutamic Acid
4	D-Glutamic Acid
5	D,L-Serine
6	Glycine
7	β-Alanine
8	γ-Amino-*n*-butyric Acid (γ-ABA)
9	D,L-β-Aminoisobutyric Acid (β-AIB)
10	D-Alanine
11	L-Alanine
12	D,L-β-Amino-*n*-butyric Acid (β-ABA)
13	α-Aminoisobutyric Acid (AIB)
14	D,L-α-Amino-*n*-butyric Acid (α-ABA)
15	D,L-Isovaline
16	L-Valine
17	D-Valine
X:	unknown

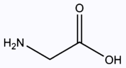
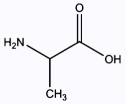
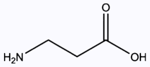
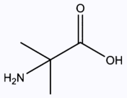
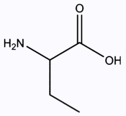
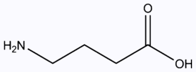
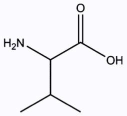
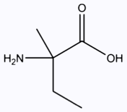
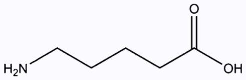
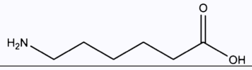
Ehrenfreund et al. (2001)

Interstellar Precursors of Meteoritic Organics?

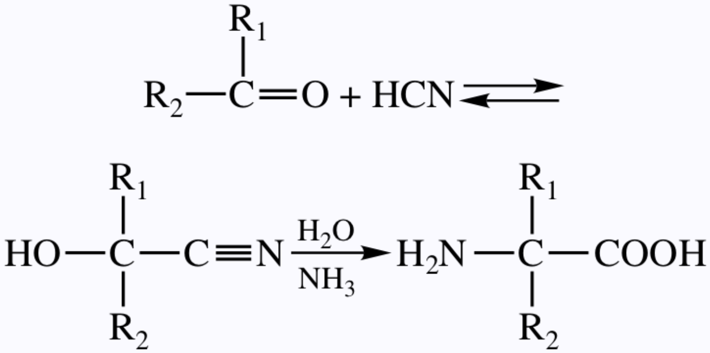
Aqueous phase reactions with H_2O, NH_3, HCN, CO, CO_2, H_2CO, CH_3CHO, CH_3COCH_3, CH_2CHCN

Amino acid stable isotopes and formation pathways 1525

Table 4. Analyzed amino acids and their structural characteristics.

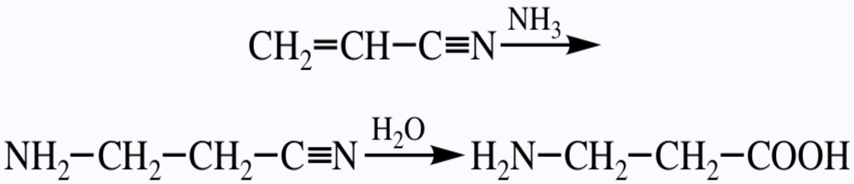
Name	Structure	Carbon number	Amine position	Alpha substituent
Glycine (Gly)		2	α	H
Alanine (Ala)		3	α	H
β-Alanine (β-Ala)		3	β	H
α-Aminoisobutyric acid (α-AIB)		4	α	CH_3
α-Aminobutyric acid (α-ABA)		4	α	H
γ-Aminobutyric acid (γ-ABA)		4	γ	H
Valine (Val)		5	α	H
Isovaline (Iva)		5	α	CH_3
δ-Amino-*n*-valeric acid		5	δ	H
ε-Amino-*n*-caproic acid		6	ε	H

Strecker synthesis:



$$R_2-\overset{R_1}{\overset{|}{C}}=O + HCN \rightleftharpoons HO-\underset{R_2}{\overset{R_1}{C}}-C\equiv N \xrightarrow[NH_3]{H_2O} H_2N-\underset{R_2}{\overset{R_1}{C}}-COOH$$

Michael addition:



$$CH_2=CH-C\equiv N \xrightarrow{NH_3} NH_2-CH_2-CH_2-C\equiv N \xrightarrow{H_2O} H_2N-CH_2-CH_2-COOH$$

Pizzarello et al. (2006)

The Meteoritical Society

Meteoritics & Planetary Science 47, Nr 9, 1517–1536 (2012)
doi: 10.1111/j.1945-5100.2012.01415.x

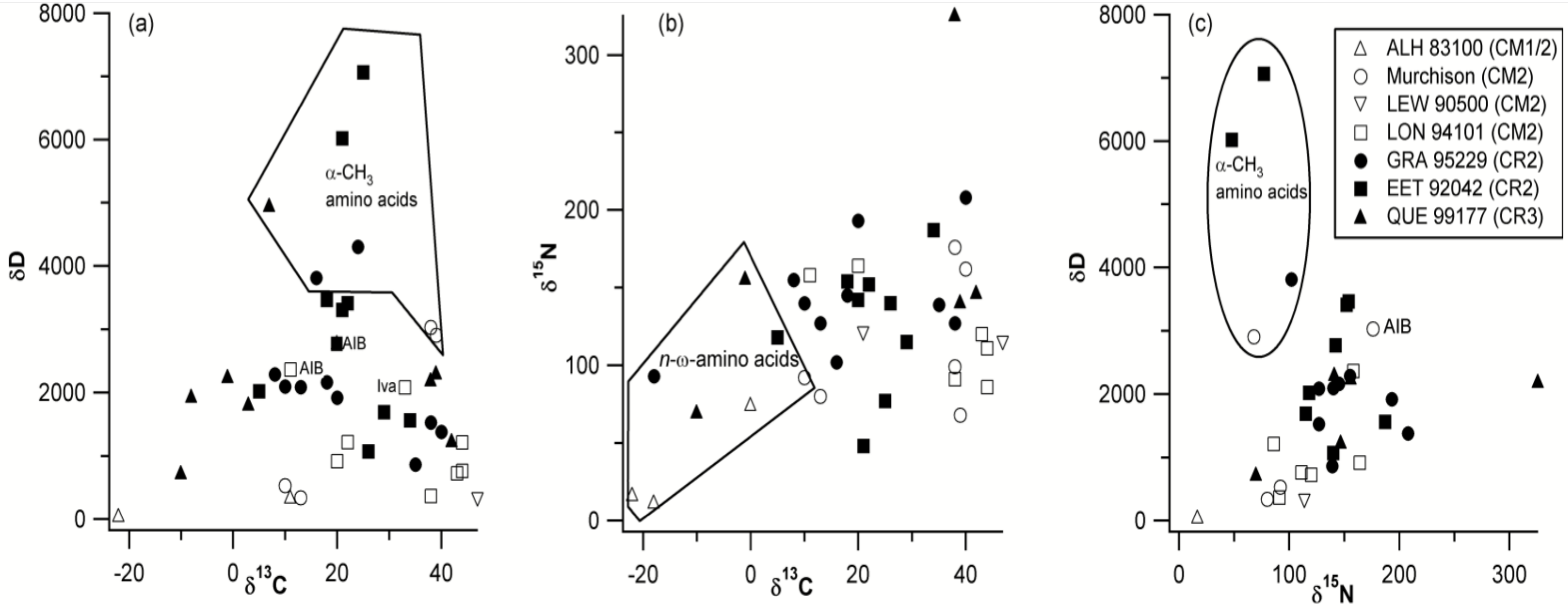
Compound-specific carbon, nitrogen, and hydrogen isotopic ratios for amino acids in CM and CR chondrites and their use in evaluating potential formation pathways

Jamie E. ELSILA[1*], Steven B. CHARNLEY[1], Aaron S. BURTON[2], Daniel P. GLAVIN[1], and Jason P. DWORKIN[1]

[1]NASA Goddard Space Flight Center and the Goddard Center for Astrobiology, Greenbelt, Maryland 20771, USA
[2]NASA Postdoctoral Program Administered by Oak Ridge Associated Universities, Greenbelt, Maryland 20771, USA
[*]Corresponding author. E-mail: jamie.elsila@nasa.gov

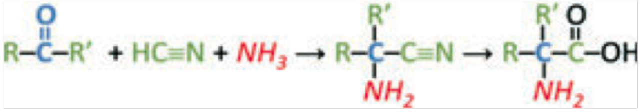
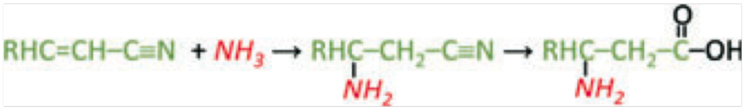
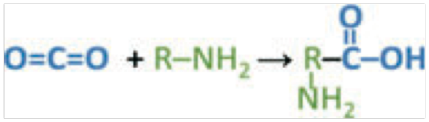
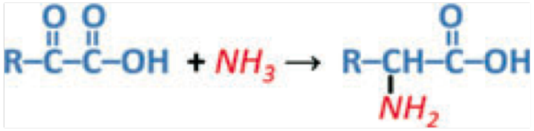
(Received 06 June 2012; revision accepted 08 August 2012)

Abstract–Stable hydrogen, carbon, and nitrogen isotopic ratios (δD, $\delta^{13}C$, and $\delta^{15}N$) of organic compounds can reveal information about their origin and formation pathways. Several formation mechanisms and environments have been postulated for the amino acids detected in carbonaceous chondrites. As each proposed mechanism utilizes different precursor molecules, the isotopic signatures of the resulting amino acids may indicate the most likely of these pathways. We have applied gas chromatography with mass



Using D, ^{15}N and ^{13}C to Probe Amino Acid Origin

Table 6. Proposed formation mechanisms and predictions.

	Predictions			
Mechanism	Amine	$\delta^{13}C$	$\delta^{15}N$	δD
I. Cyanohydrin (Strecker)  $R-\overset{\overset{O}{\Vert}}{C}-R' + HC\equiv N + NH_3 \rightarrow R-\underset{NH_2}{\overset{R'}{C}}-C\equiv N \rightarrow R-\underset{NH_2}{\overset{R'}{C}}-\overset{\overset{O}{\Vert}}{C}-OH$	α	Lower enrichment in longer chains	Enriched	Higher enrichment with more H atoms
II. Michael addition  $RHC=CH-C\equiv N + NH_3 \rightarrow RH\underset{NH_2}{C}-CH_2-C\equiv N \rightarrow RH\underset{NH_2}{C}-CH_2-\overset{\overset{O}{\Vert}}{C}-OH$	Mostly β (no α)	Lower enrichment, independent of length	Enriched	Less enriched than Strecker
III. CO_2 addition  $O=C=O + R-NH_2 \rightarrow \underset{NH_2}{R}-\overset{\overset{O}{\Vert}}{C}-OH$	Any	Lower enrichment in longer chains	Potentially higher than other mechanisms	Enriched
IV. Reductive amination  $R-\overset{\overset{O}{\Vert}}{C}-\overset{\overset{O}{\Vert}}{C}-OH + NH_3 \rightarrow R-\underset{NH_2}{CH}-\overset{\overset{O}{\Vert}}{C}-OH$	Any mono-alkyl	Higher enrichment, independent of length	Enriched	Higher enrichment with more H atoms

Blue/bold represents material from ^{13}C-enriched CO; green represents material derived from the “carbon isotope pool.” Ammonia-derived nitrogen is shown in red/italics.

Elsila et al. (2012)

ISM-Solar System Isotopic Connection?

- For comet composition, good correlation with known interstellar molecules (but CH_3OH low etc.)

- Ice CHO compositions both consistent with grain chemistry at ~10K

- Isotopes suggest comets contain volatile materials with different thermal histories: ~25-35K (D/H in water); ~10K (^{15}N in HCN, CN and ammonia)

- Apparent retention of `interstellar’ chemical characteristics - variable mixing and re-processing in the nebula (81P/Wild 2 vs. Hale Bopp vs. 67P)

- Interstellar isotopic measurements may provide insight into the starting materials for a prebiotic chemistry initiated by comets and asteroids/meteorites

ACKNOWLEDGEMENTS

Eva Wirstroem, Gilles Adande, Stefanie Milam
&
Jamie Elsila-Cook, Jose Aponte, Michael Mumma

END