Cometary volatiles

Les Houches 2017

Dominique Bockelée-Morvan

l'Observatoire de Paris — LESIA

Laboratoire d'Études Spatiales et d'Instrumentation en Astrophysique

Comets

- **Primitive icy bodies :**

  remnants of the small bodies which formed the outer planets

- **Chemical composition :**

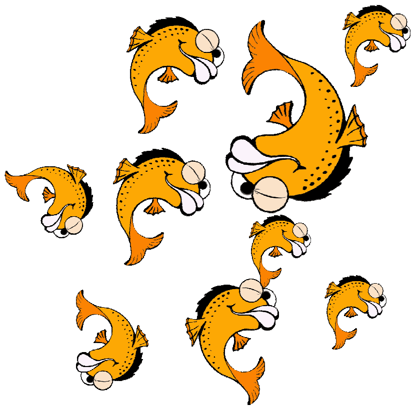
  that of the solar nebula, the Solar proto-planetary disk

- **Clues to :**
  - Solar System formation and evolution
  - Origin of the volatiles in telluric planets
  - Origin of Earth oceans

- **Two reservoirs of comets:**
  - Oort cloud
  - Kuiper Belt

152 years of comet spectroscopy

28 molecules
40 atoms, radicals, ions



Isotopes

Space exploration of comets

Comet	Mission	Date	Distance	Velocity
21P/Giacobini-Zinner	ICE	11 Sep.1985	7800 km	21 km/s
1P/Halley	VEGA 1	6 Mar.1986	8890 km	79 km/s
1P/Halley	Suisei	8 Mar.1986	150 000 km	
1P/Halley	VEGA 2	9 Mar.1986	8030 km	77 km/s
1P/Halley	Sakigake	11 Mar.1986	7 000 000 km	
1P/Halley	**Giotto**	**14 Mar.1986**	**596 km**	**68 km/s**
26P/Grigg-Skjellerup	Giotto	10 July 1992	200 km	14 km/s
19P/Borrelly	Deep Space 1	22 Sep.2001	2170 km	17 km/s
81P/Wild 2	Stardust	2 Jan.2004	236 km	6 km/s
9P/Tempel 1	Deep Impact	4 July 2005	30-500 km	11 km/s
103P/Hartley 2	EPOXI	4 Nov.2010	694 km	12 km/s
9P/Tempel 1	Stardust-NEXT	15 Feb. 2011	181 km	11 km/s

67P/Churymov-Gerasimenko	**Rosetta**	**2014-2016**	**0- 50 km**	**< 0.1 km/s**

Outline

- Review cometary ice molecular composition
  - ✓Volatile composition from spectroscopy
  - ✓Chemical diversity
  - ✓New findings from Rosetta
  - ✓Formation mechanisms of cometary volatiles
- Isotopic composition : H, N, O

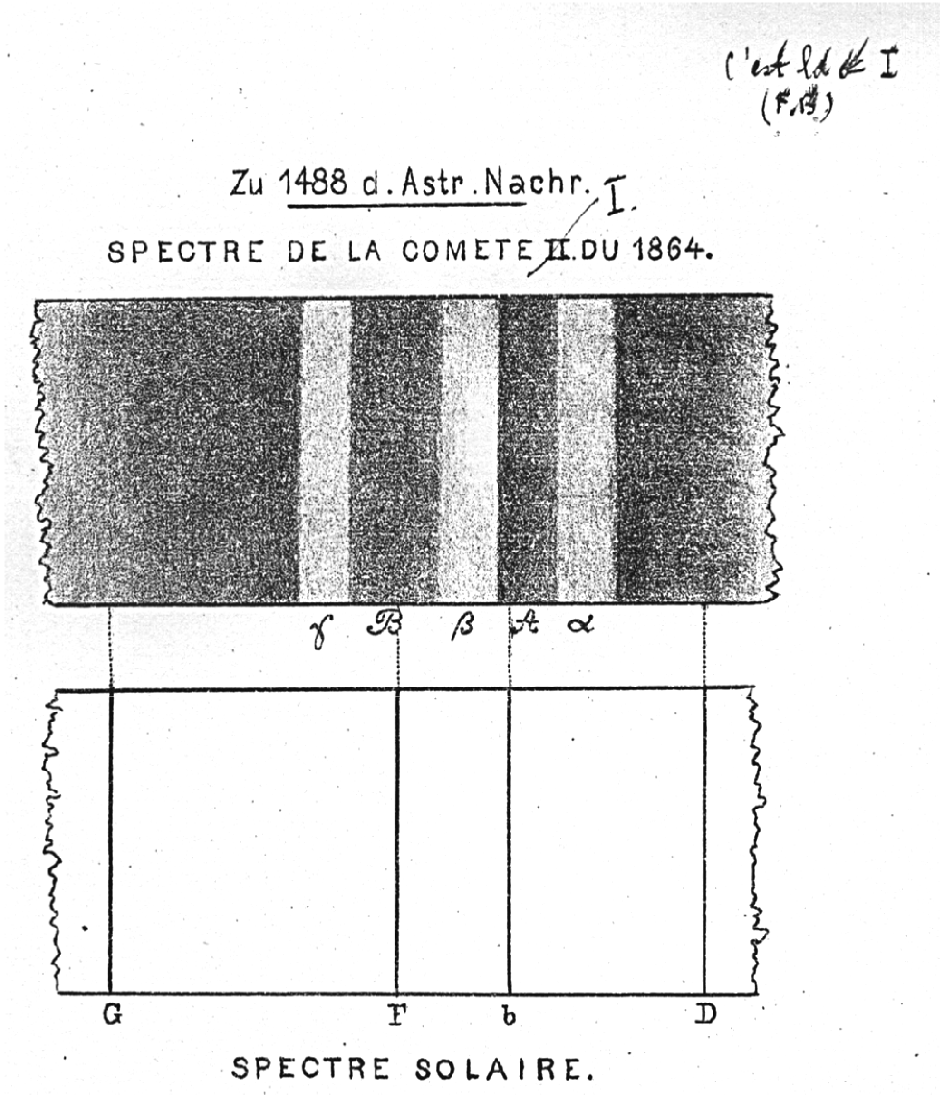
Spectroscopic investigations of cometary volatiles

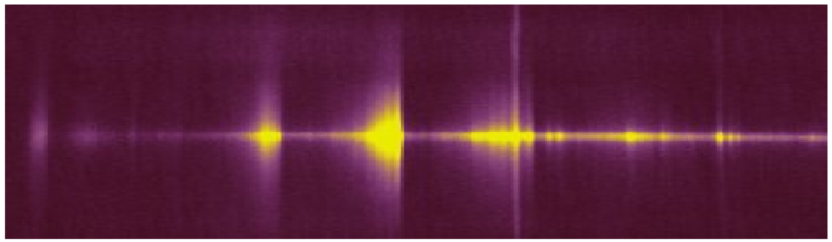
First comet spectrum observed by G. B. Donati

C/1864 N1 (Tempel)

Donati, 1864, *Astron. Nachr.*, **62**, 375

Giovanni Donati (1826—1873}





C/2001 A2 (LINEAR)
réseau + caméra CCD
© C. Buil

Spectroscopy of cometary atmospheres

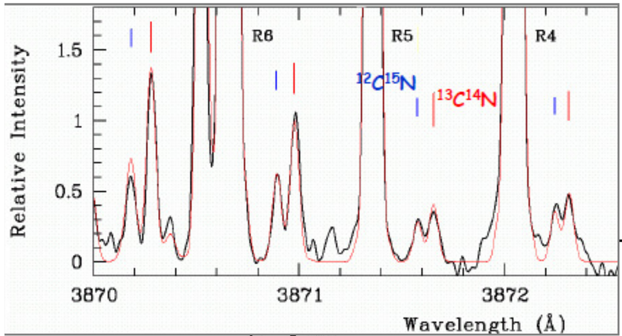
❖ **From the UV to the radio**

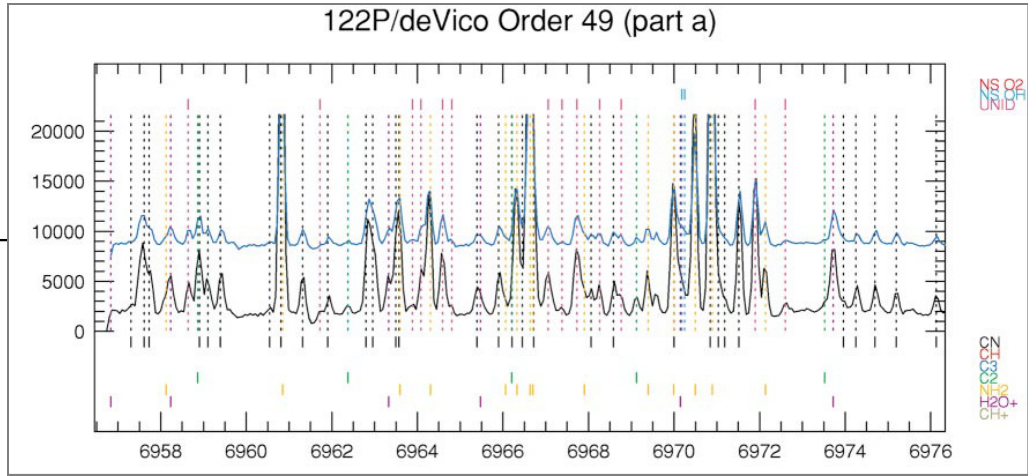
❖ **Main excitation/emission processes**

- Fluorescence emission pumped by Solar Radiation
  parent & daughter species
- Prompt emission : e.g. O^1D (visible), OH* (IR)
- Electron impact excitation
- Collisional excitation

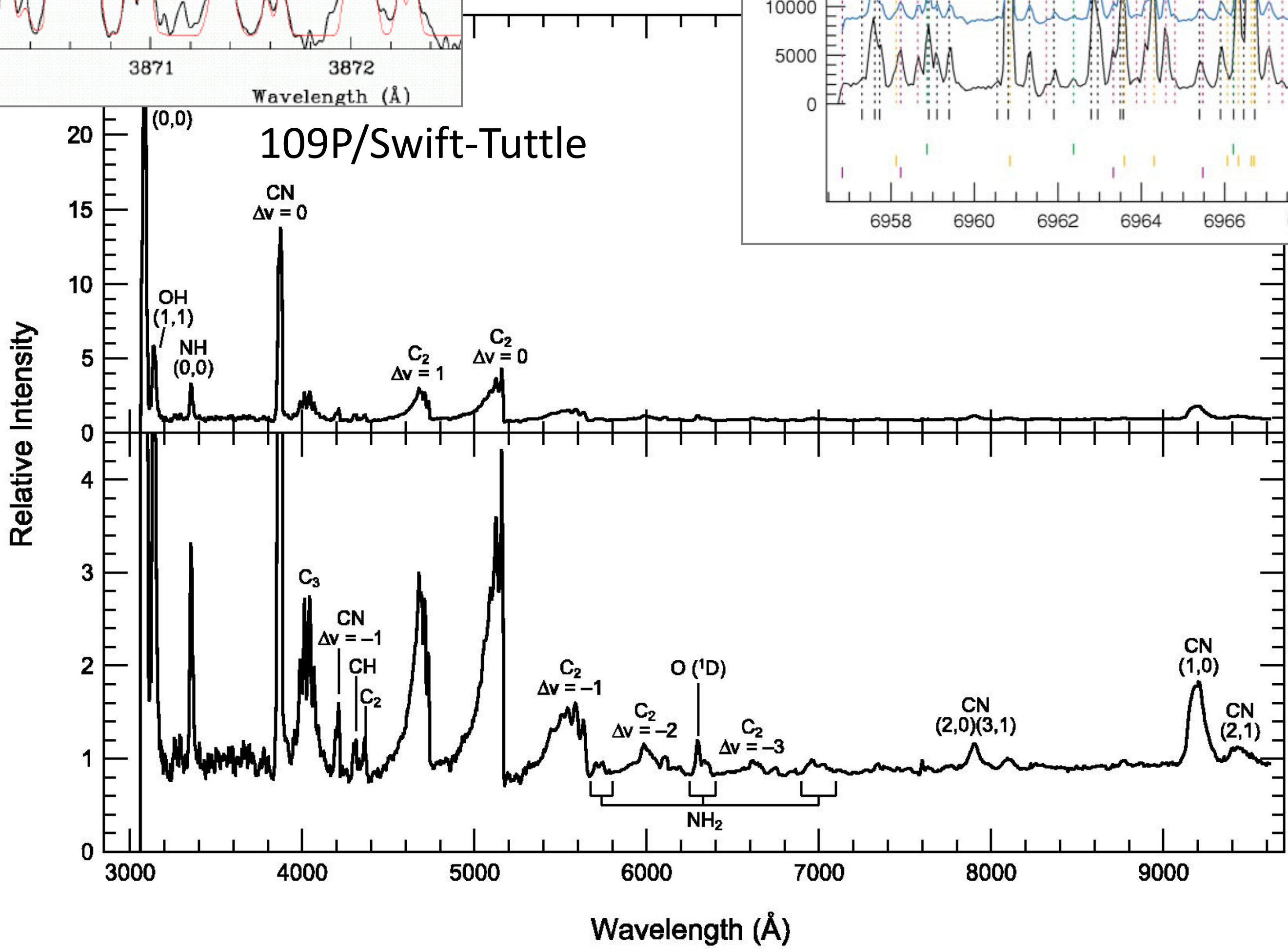
Visible spectroscopy

Hutsemekers et al. 2005





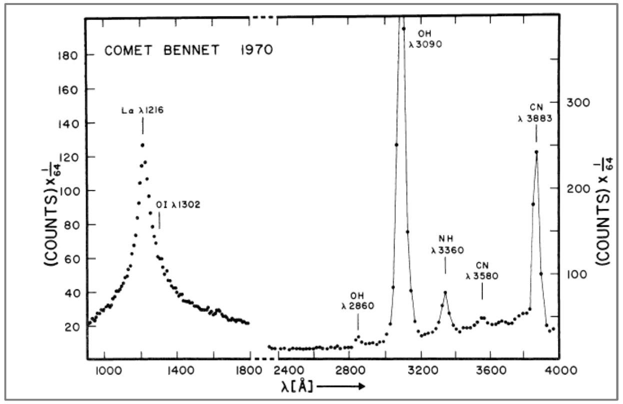
Cochran & Cochran 2002



Feldman et al. 2004

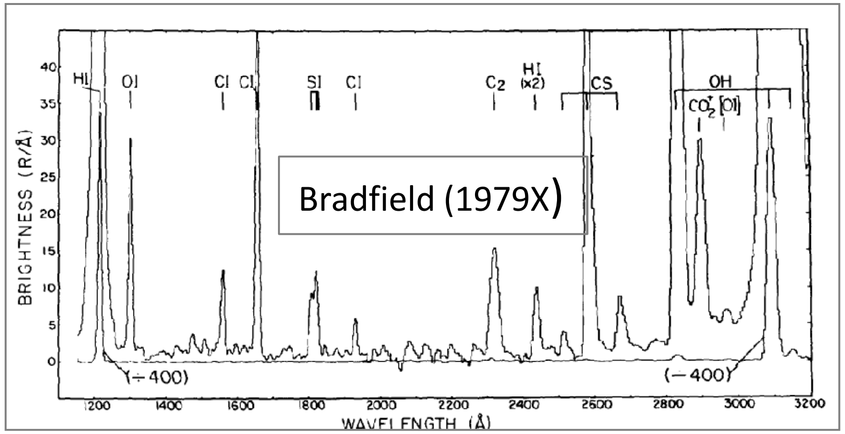
UV spectroscopy

OAO-2/NASA: First UV spectrum of a comet



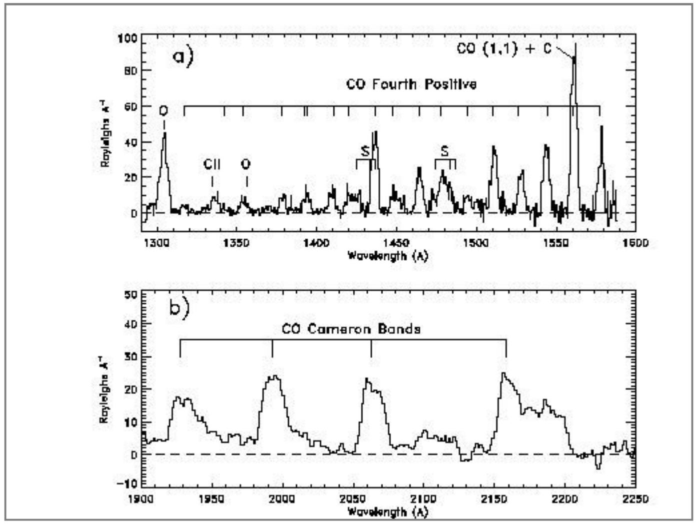
Code et al. 1972

International Ultraviolet Explorer: 1978-1996



Weaver et al. 1981

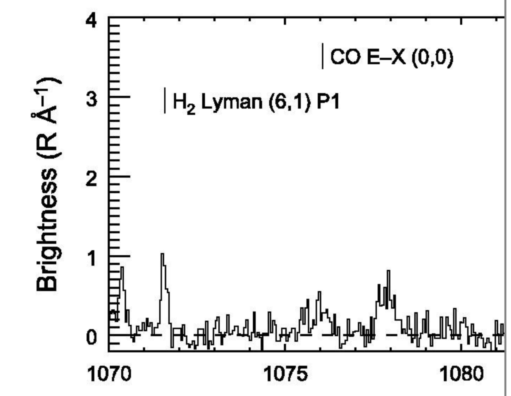
HST: C/1996 B2 (Hyakutake)



Weaver et al. 1998

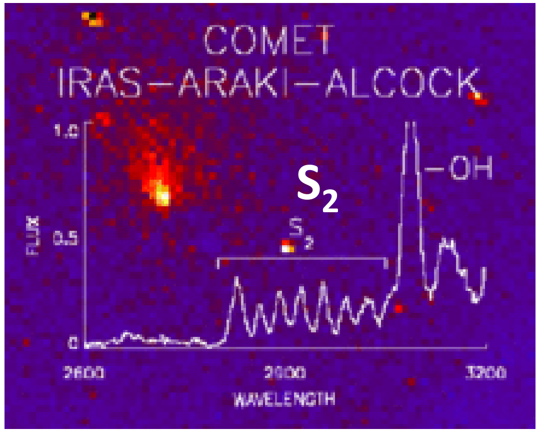
FUSE:

C/2001 A2 (LINEAR)



Feldman et al. (2002)

IUE

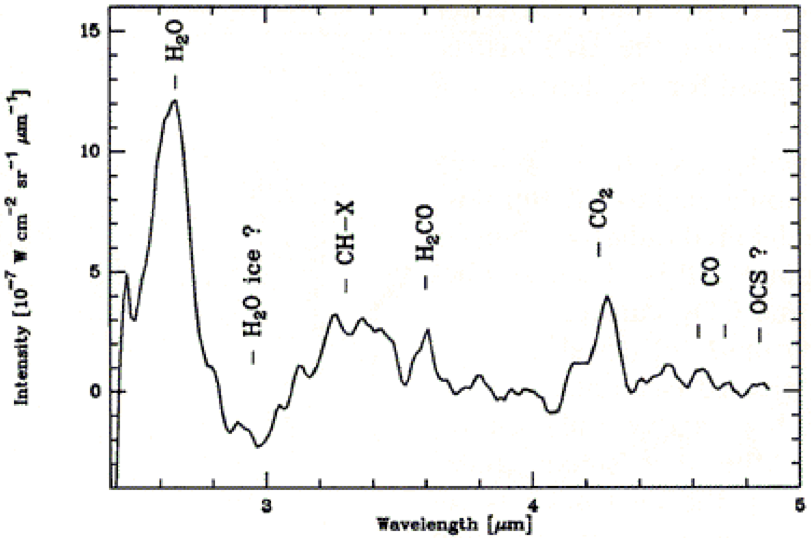


radicals	OH, CH, NH, NH_2 CN, C_2, C_3, CS, NS, SO CN, $C^{13}C$, $C^{15}N$, $C^{34}S$
atoms	H, O, C, S Na, K*, Cr*, Ca*, Mn* Fe*, Ni*, Cu*, Co*, V*
ions	O^+, C^+, Ca^{+*} H_2O^+, H_3O^+, OH^+ CO_2^+, CO^+, HCO^+ CH^+, N_2^+

* only in sungrazing comets

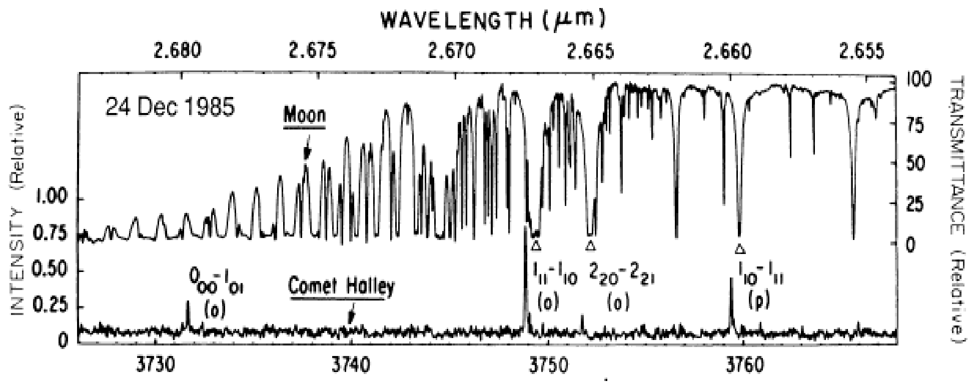
Infrared spectroscopy

IKS/VEGA: 1P/HALLEY



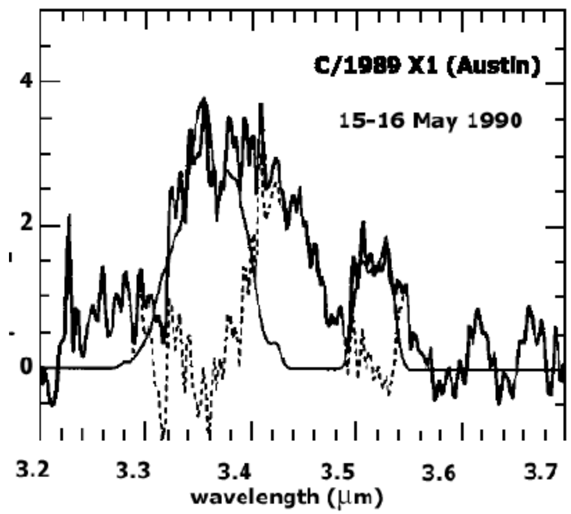
Combes et al. (1986)

KAO: 1P/HALLEY – First detection of water

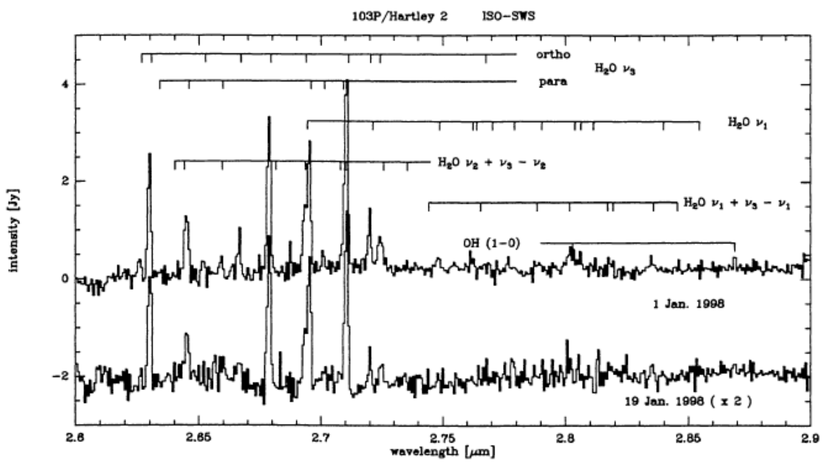


Mumma et al. (1986)

CH_3OH : main contributor of 3.4 μm band

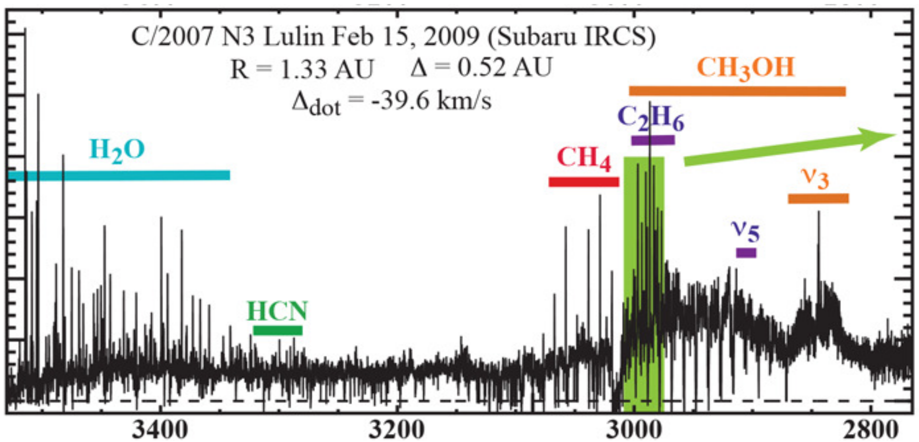


ISO : water in 103P/Hartley 2



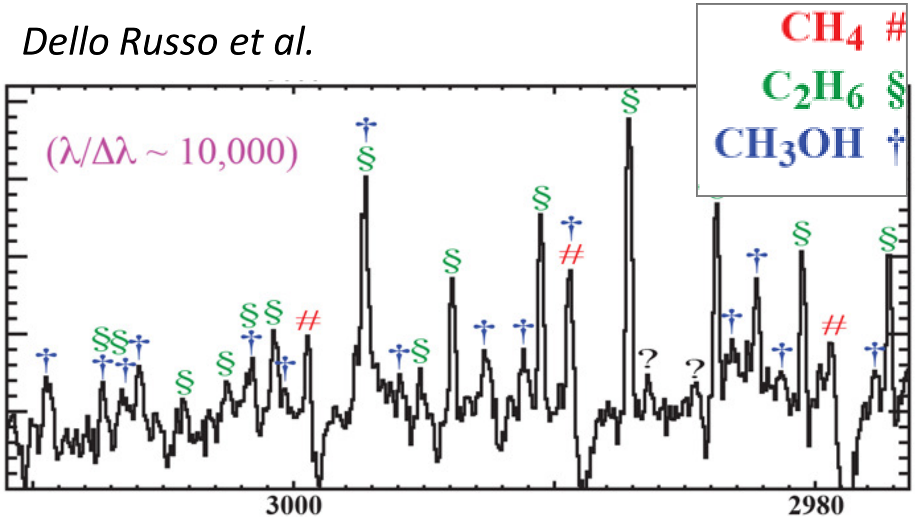
Infrared spectroscopy (High Res)

IRTF and 10-m class telescopes



Wavenumber (cm-1)

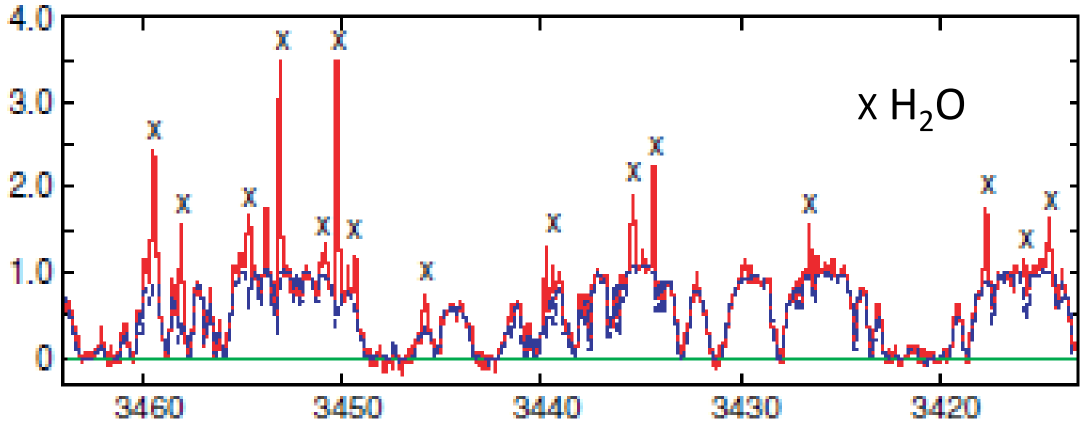
Dello Russo et al.



Wavenumber (cm-1)

Detected molecules in near IR:
H_2O, OH*
CH_4, C_2H_2, C_2H_6
CO, CH_3OH, H_2CO
NH_3 , HCN

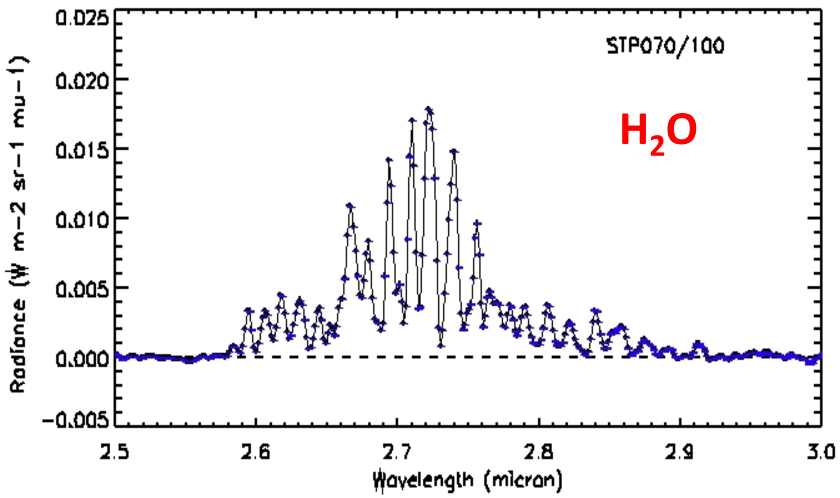
Kawakita et al. 2009, Keck II, C/2004 Q2

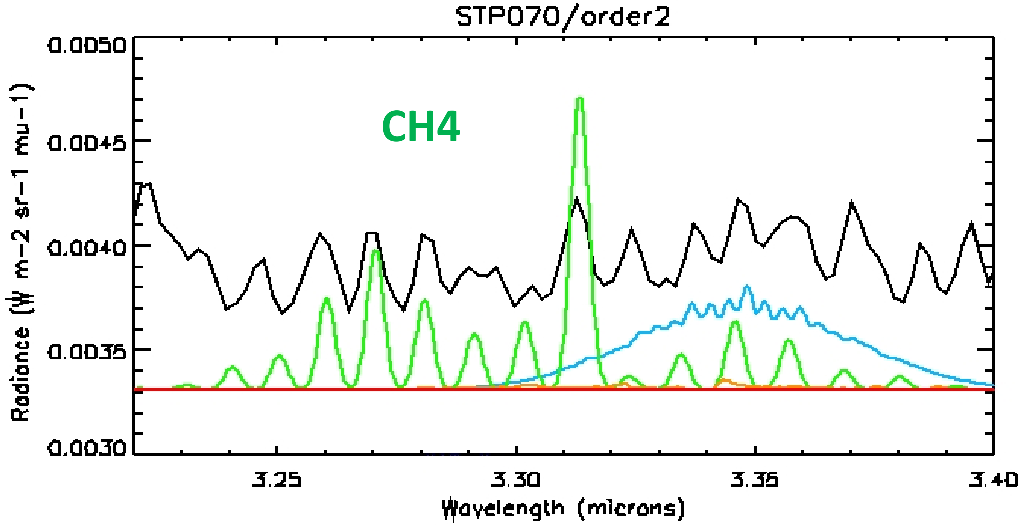


Wavenumber (cm-1)

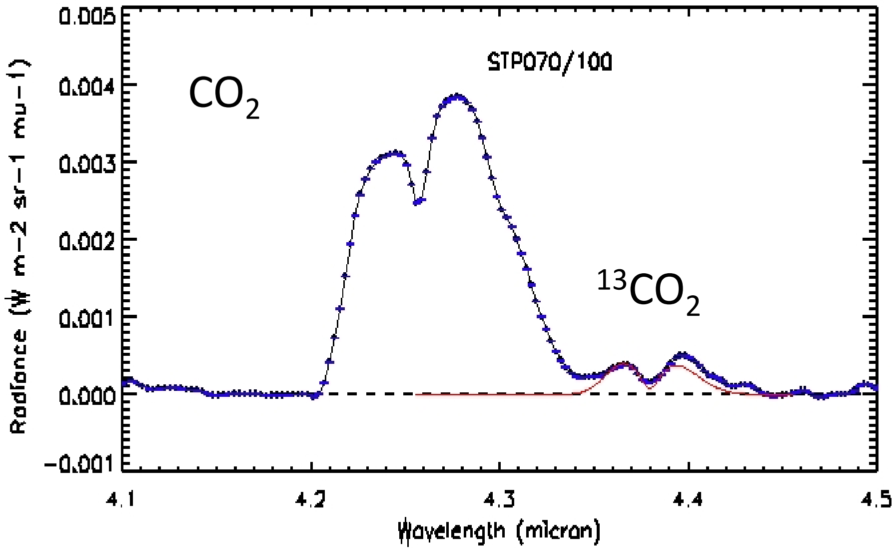
Rosetta/VIRTIS-H spectra at perihelion

Order 4





Order 0

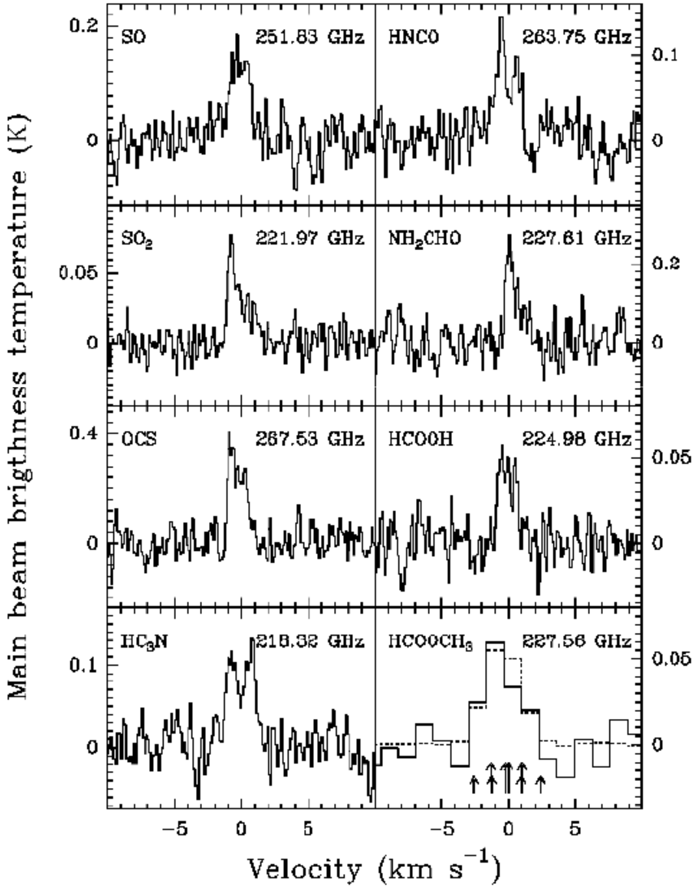


Bockelée-Morvan et al. 2016

Millimeter/Submillimeter spectroscopy

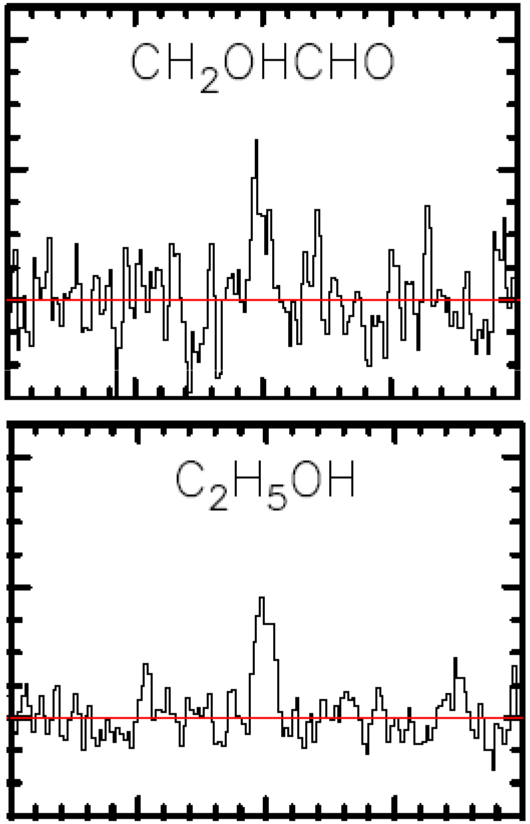
23 molecules detected starting with HCN in comet Kohoutek

C/1995 O1 (Hale-BOPP)



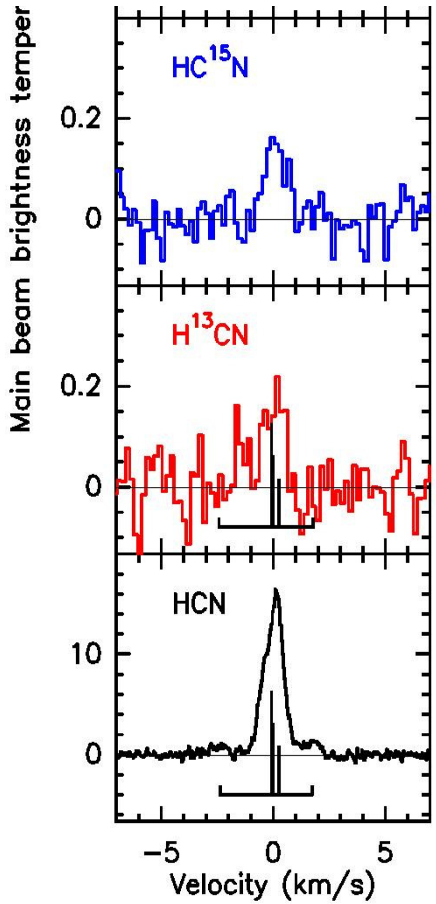
Bockelée-Morvan et al. 2000

C/2014 Q2 (Lovejoy)



Biver et al. 2015

17P /Holmes

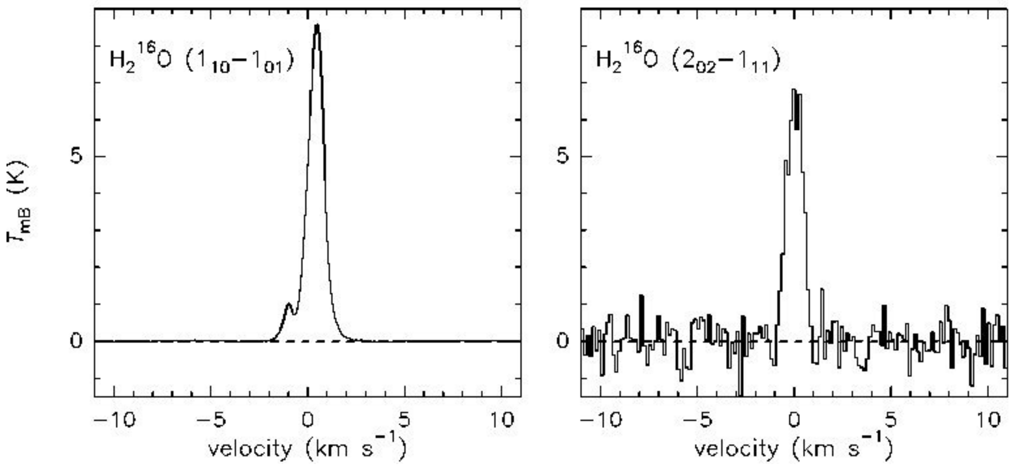


Bockelée-Morvan et al. 2008

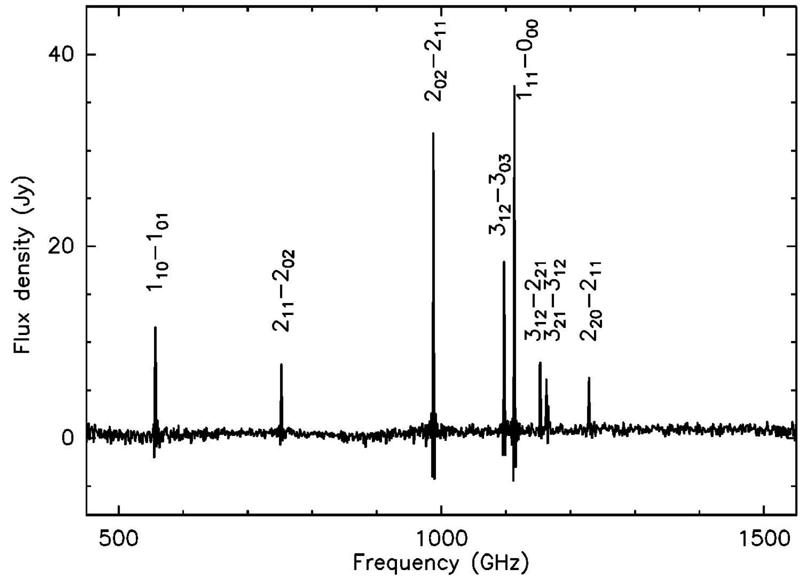
Observation of water vapor

Submillimeter, far-IR : SWAS, Odin, Herschel, MIRO/Rosetta

Herschel/HIFI , comet C/2009 P1



Herschel/SPIRE comet 103P



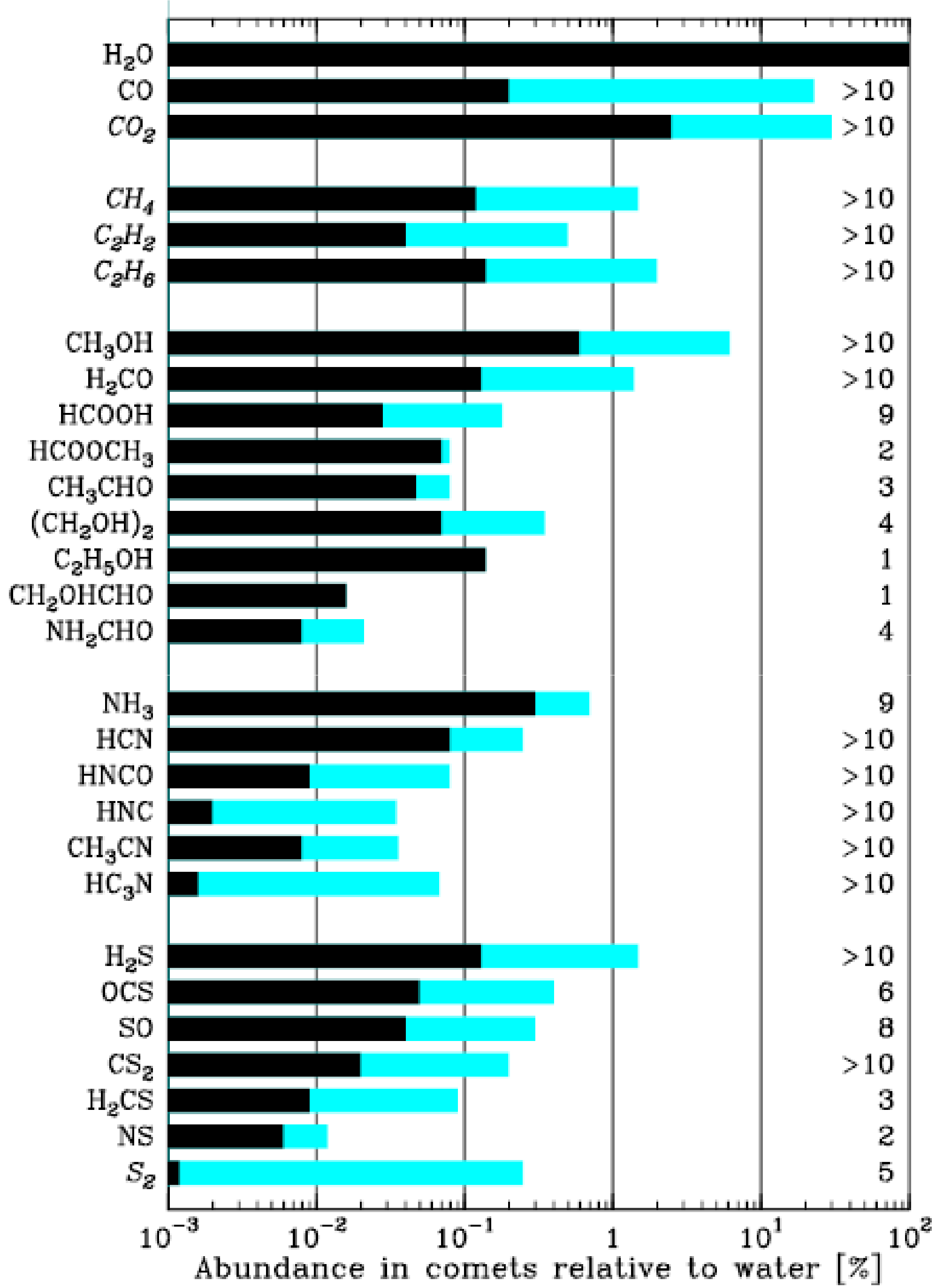
Bockelée-Morvan et al. 2012

Molecular composition

Comet composition based on spectroscopy

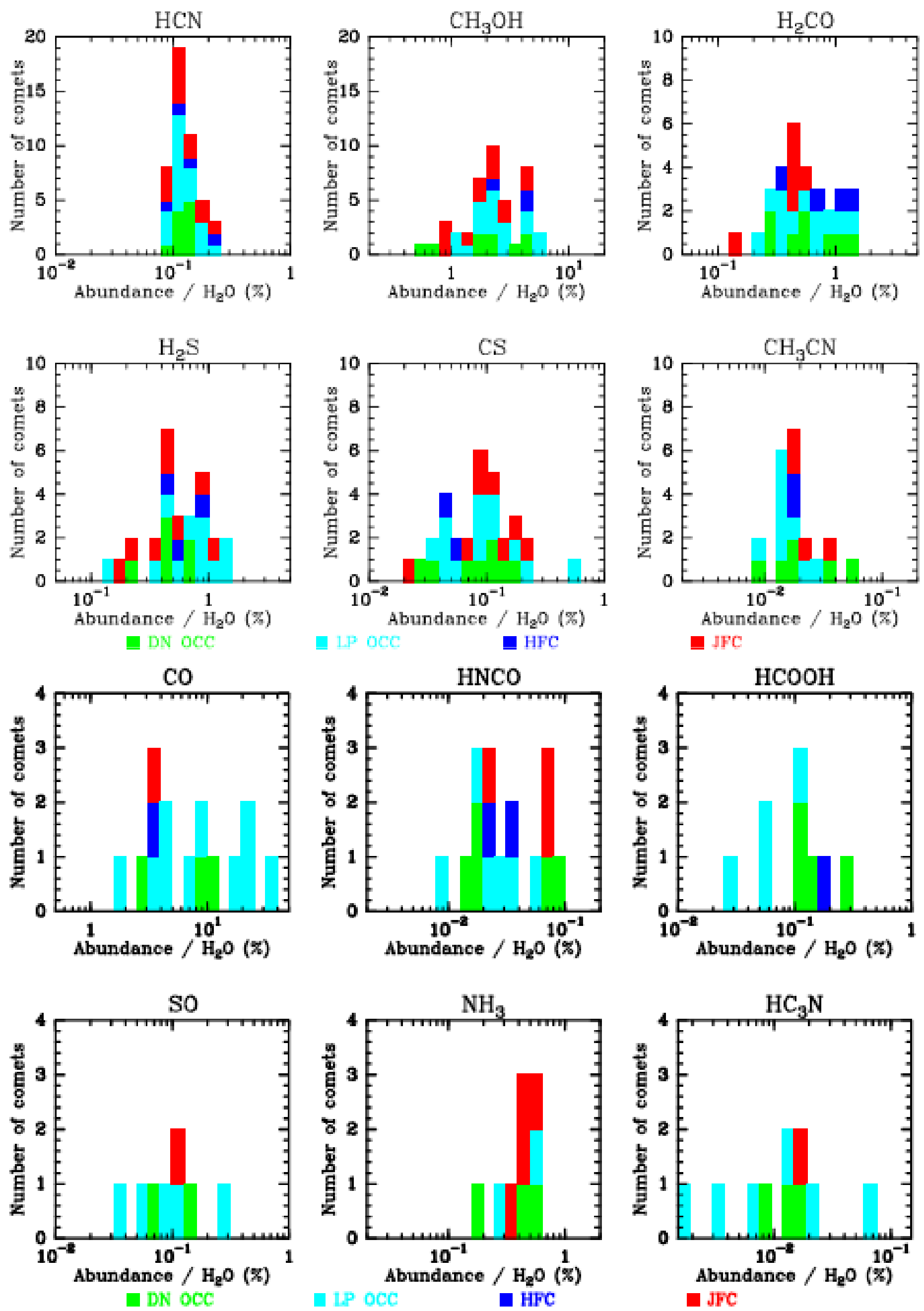
- 28 molecules detected
- Several complex organics now detected in several comets
- Complex molecules are abundant

- Diversity in relative abundances for both Oort cloud & Kuiper-Belt comets



Composition diversity in cometary atmospheres

- Plot based on mm/submm measurements
- Similar results for molecules observed in the IR



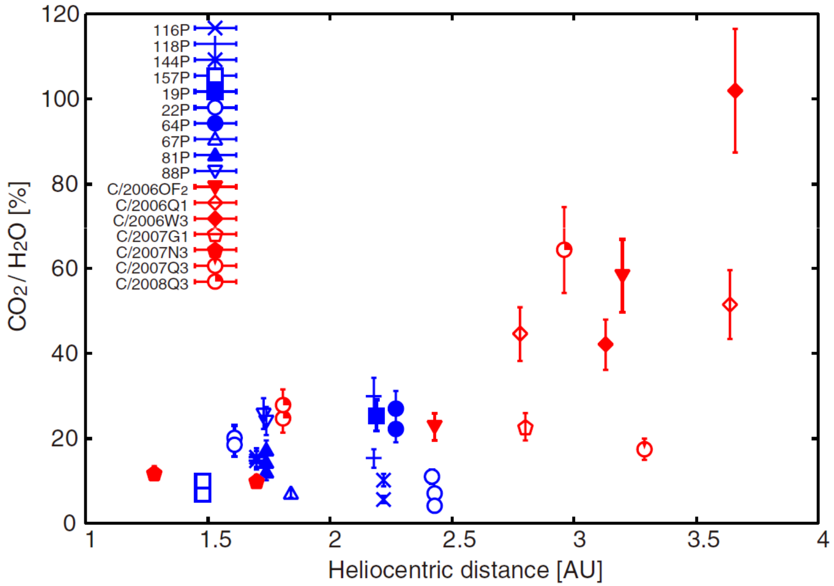
For most molecules:

- same diversity and mean abundances in the diverse dynamical populations
- Suggest formation in the same regions of the early solar system

Bockelée-Morvan & Biver, 2016, Phil. Tr.

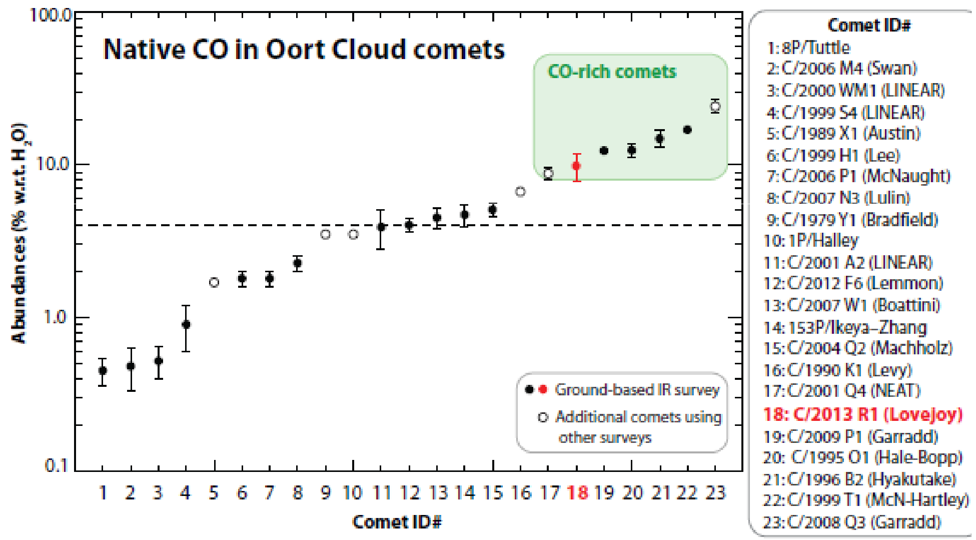
Composition diversity : CO, CO_2

CO_2 : AKARI infrared observations



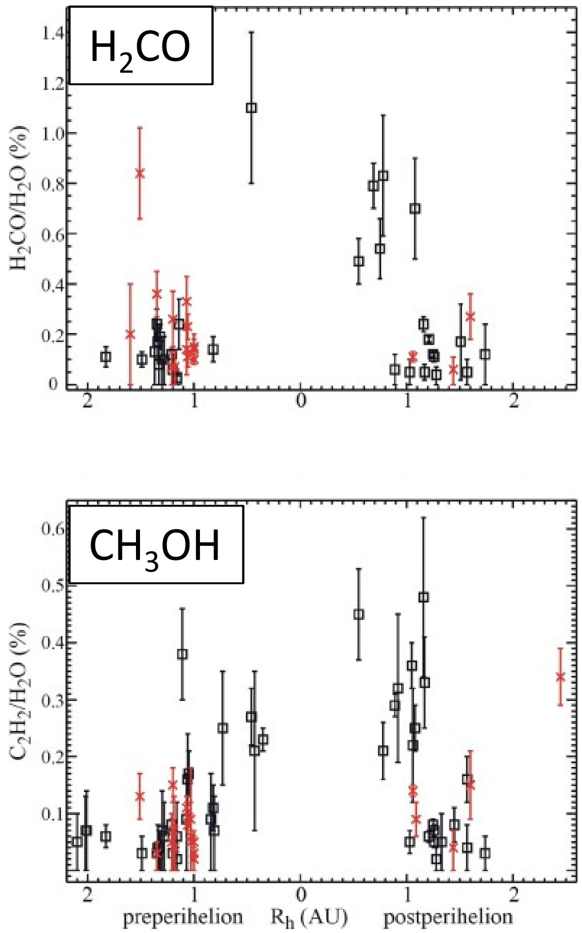
Ootsubo et al. 2012

CO : Ground based IR observations



Paganini et al. 2014

Distributed sources of gases

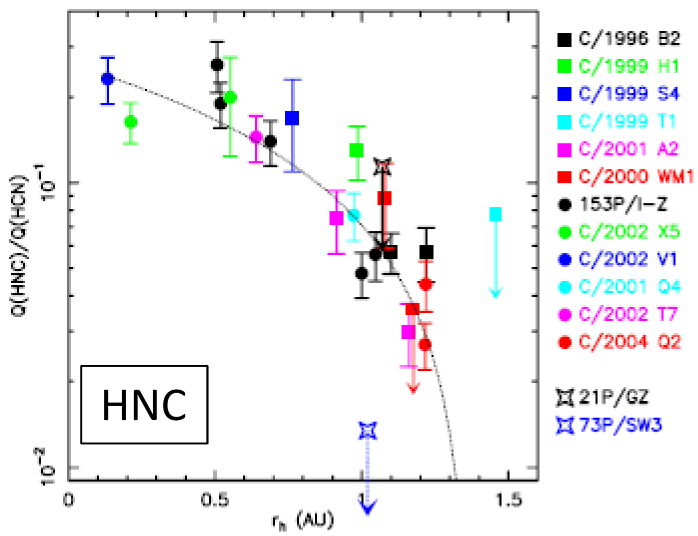


•Relative abundances increase with decreasing heliocentric distance: HNC, H2CO, NH3, CH3OH, CS

•Spatial distribution not consistent with release from the nucleus: HNC, H2CO

•Thermal degradation of macro organic molecules :

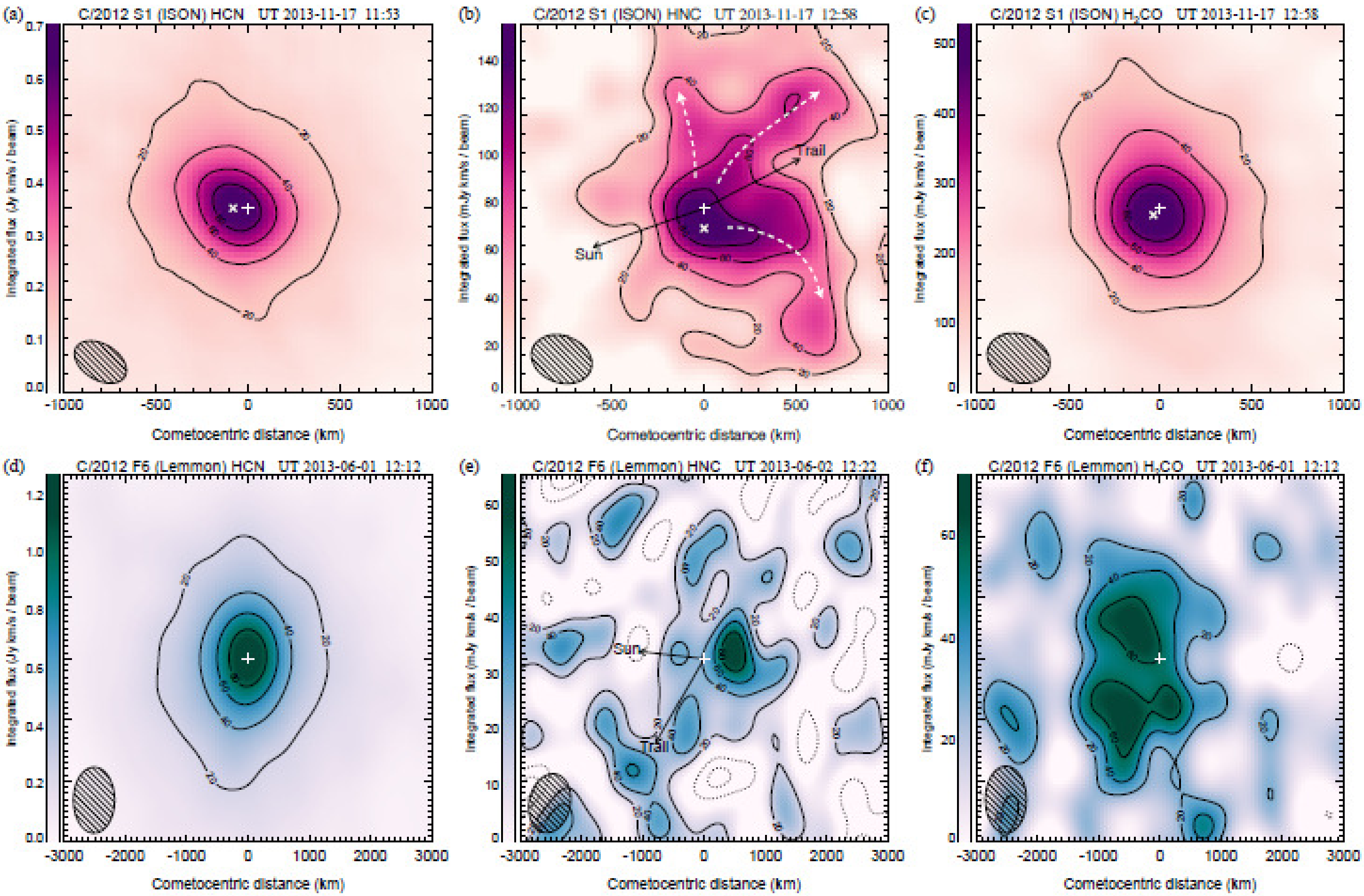
Experiments on H_2CO and HCN polymers



Dello Russo et al. 2016

Lis et al. 2007

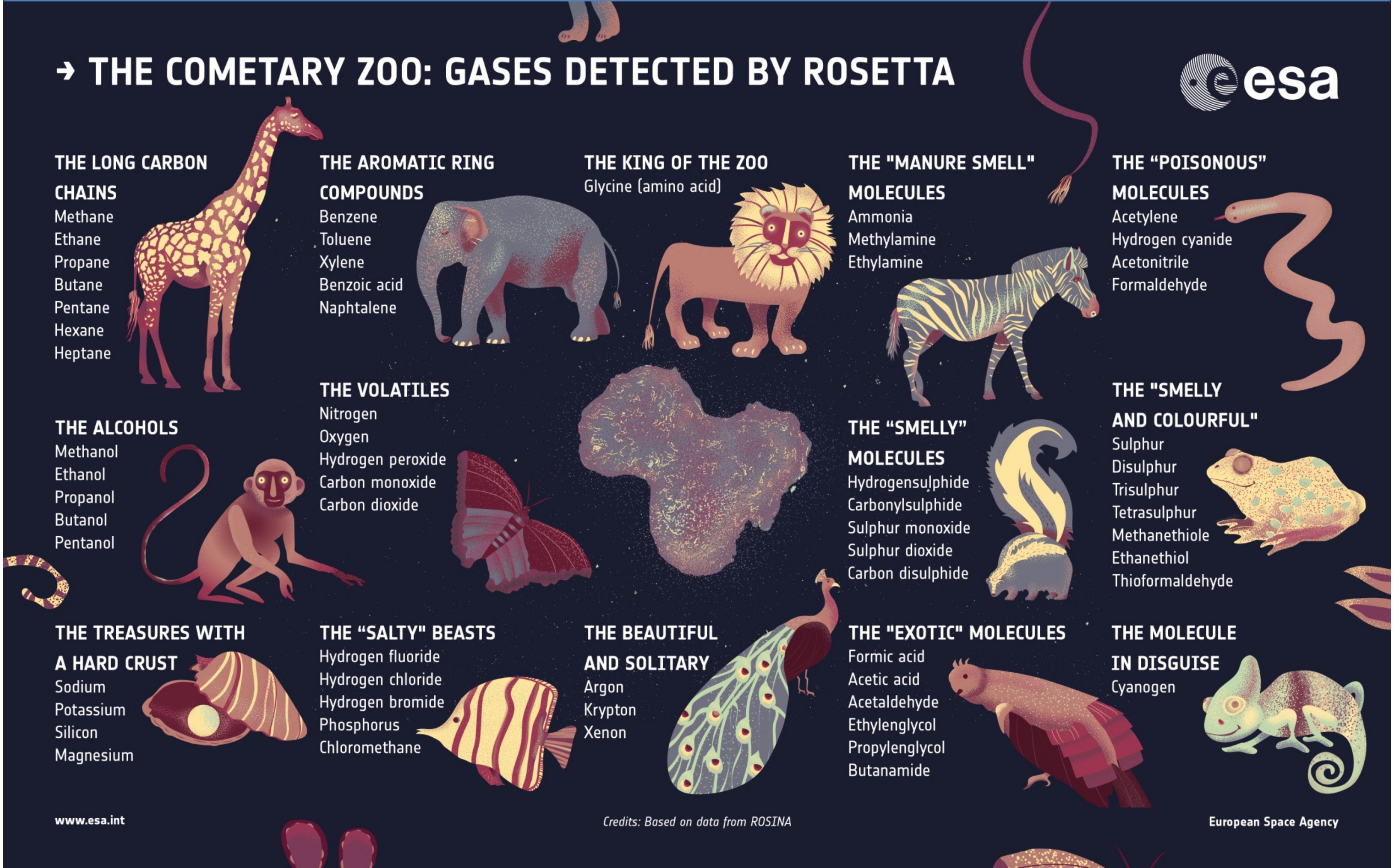
Distributed sources of H_2CO and HNC



Cordiner et al. 2014

ALMA observations

New findings from Rosetta on cometary volatiles



Gas phase compounds detected by the Rosina mass spectrometer onboard Rosetta
Copyright: ESA/Rosina team

Detection of glycine and amines in comet 67P

Altwegg et al. 2015, Science Advance

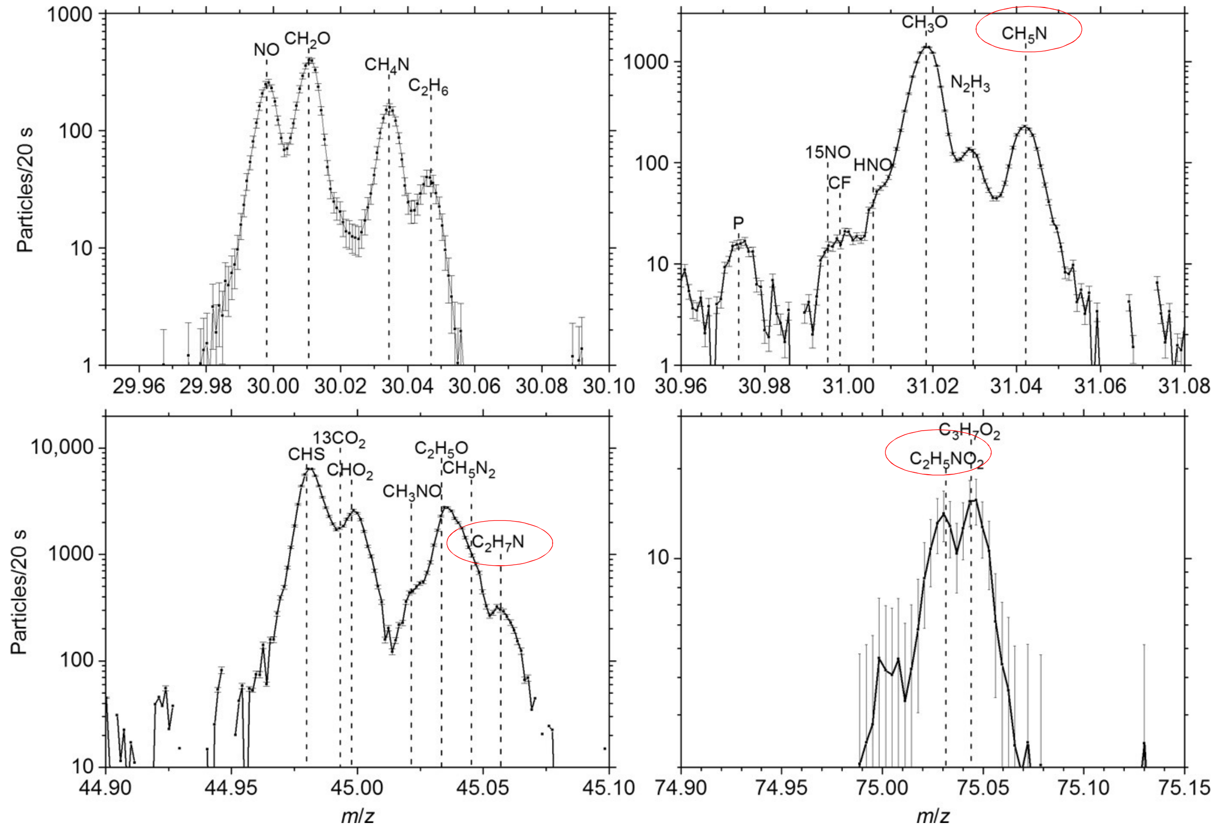
- Glycine ($C_2H_5NO_2$)
- Methylamine (CH_5N)
- Ethylamine (C_2H_7N)

Abundance ratios:

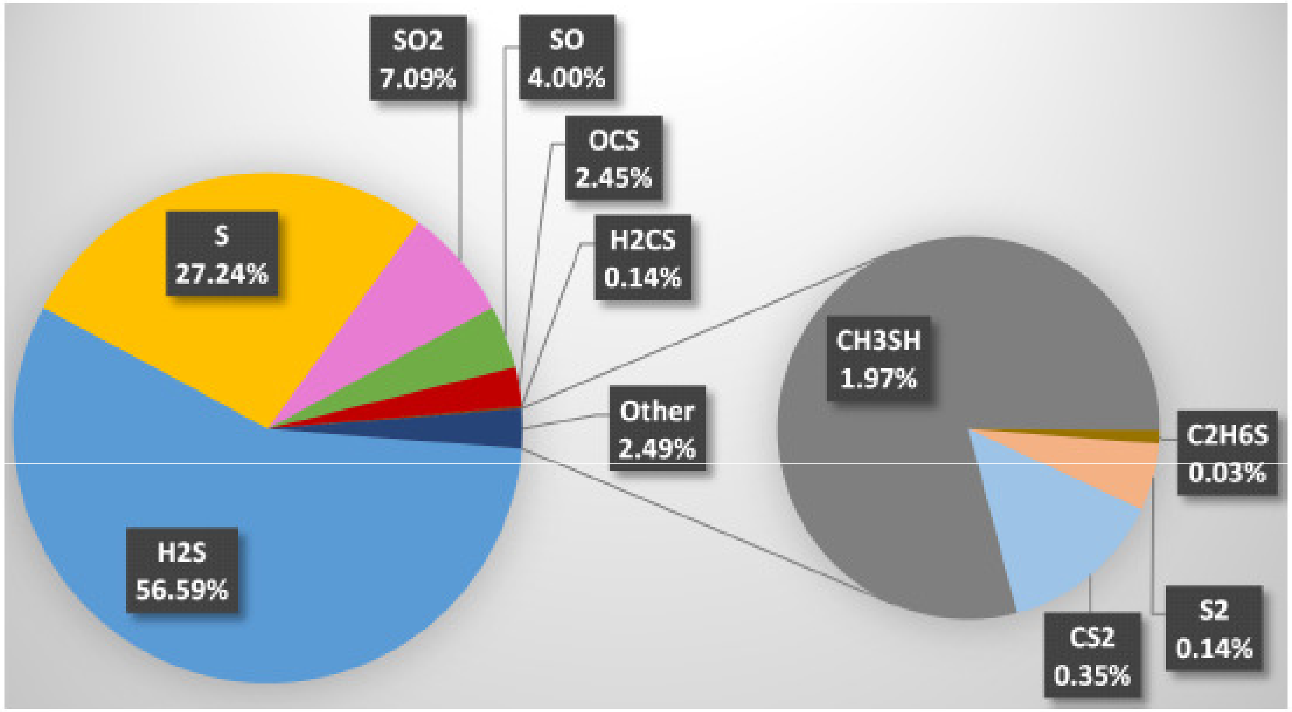
Meth/Gly= 1 +/- 0.5

Eth/Glyc = 0.3 +/- 0.2

- **Glycine radial distrib. consistent with production from heated grains**
- **Other amino acids (as alanine) not found**
- **Amino acids other than glycine need liquid water to form**
- **Formation of glycine by radical addition mechanisms on icy grains in the solar nebula or presolar cloud**



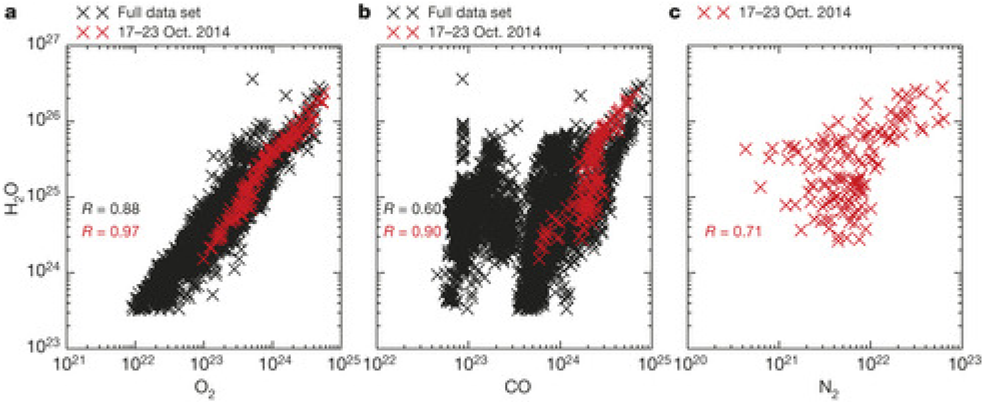
Sulfur chemistry in comet 67P



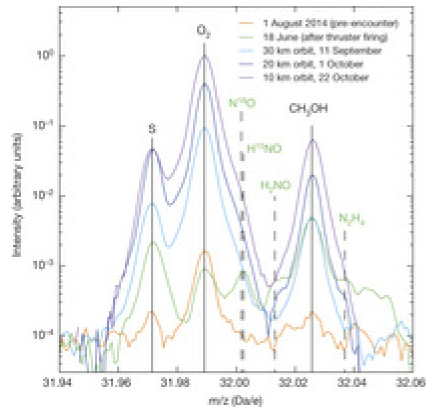
Calmonte et al. 2016

- **Detection of atomic sulfur, unknown origin**
- **SO present as parent species**
- **Detection of S_2, S_3, S_4**
  - **S_2 has very short lifetime: if formed in the pre-solar cloud, this implies that interstellar ices in condensed form were incorporated in comets**
  - **Formed by radiolysis of H_2S ? But high amounts of S_2H & H_2S_2 are formed during radiolysis contrarily to what is measured**

Large abundance of O_2



Species	Relative Abundance 1P/Halley	Relative Abundance 67P/Churyumov–Gerasimenko
H_2O	100%[a]	100%[a]
O_2	3.7 ± 1.7%[b]	3.80 ± 0.85%[c]



- **Unexpected discovery**
- O_2 abundance of 4% in 67P (Bieler et al. 2015)
- O_2 found in 1P/Halley from a reanalysis of Giotto data (Rubin et al. 2015)
- **O_2 production correlated with water production**
- Uncorrelated with highly-volatile species (N_2, CO, CO_2)

- **Proposed formation mechanism**
  - **through radiolysis of H_2O ice by cosmic rays** in the presolar cloud (Mousis et al. 2016) (radiolysis is not fast enough for formation in the solar nebula)
  - **dark cloud chemistry** (gas-phase + grain chemistry) with moderate T, and high H/O and density conditions (Taquet et al. 2016)
  - **through dismutation of H_2O_2** (Dulieu et al. 2016) : 2x H_2O_2->O_2+2xH_2O

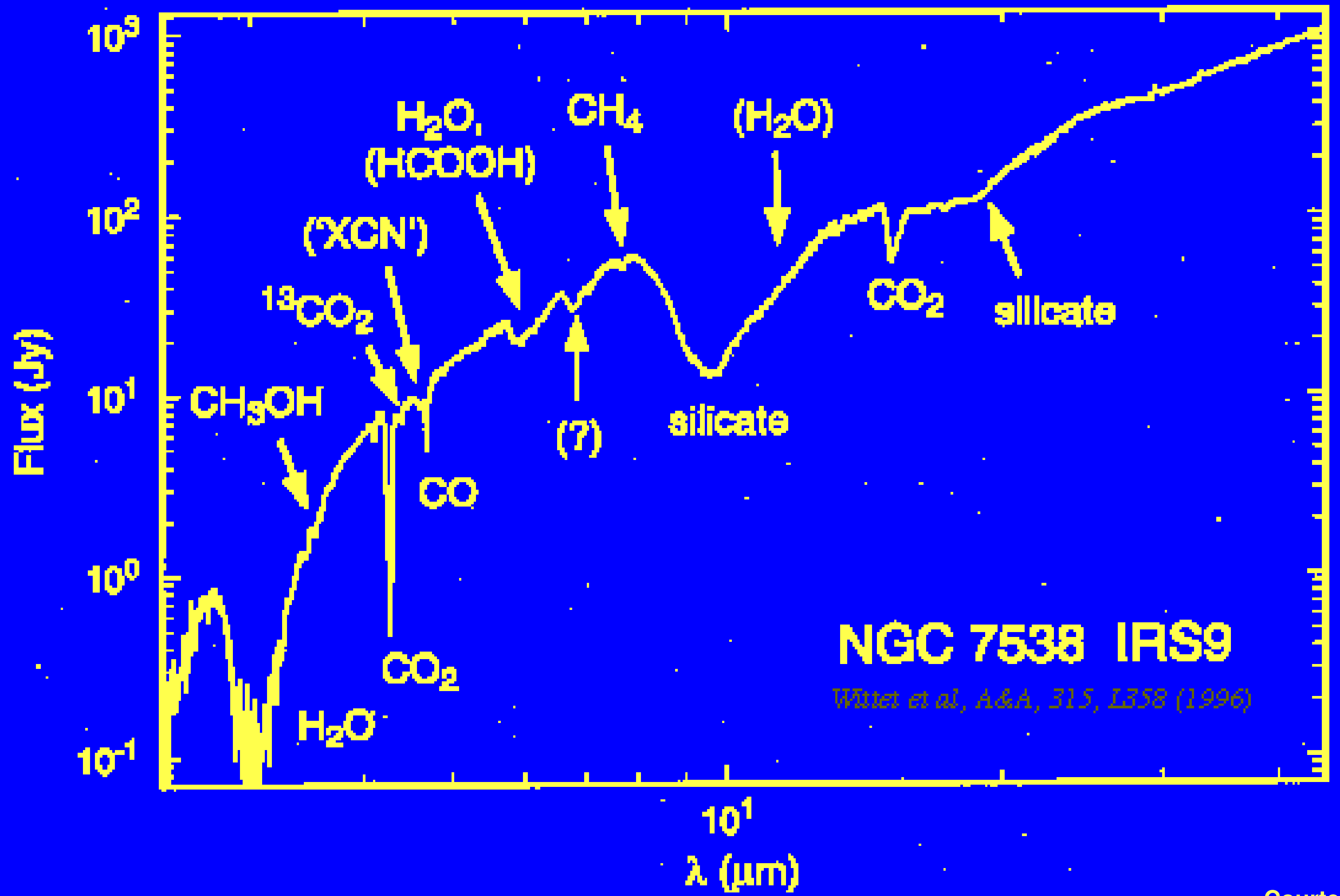
Origin of cometary volatiles

About 180 interstellar/circumstellar identified molecules

Number of Atoms										
2	3	4	5	6	7	8	9	10	11	12+
H_2 •	C_3 •	c-C_3H	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N?	HC_9N	C_6H_6
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$ •	CH_3CH_2CN	$(CH_3)_2CO$		$HC_{11}N$
AlCl	C_2O	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_3COOH?	$(CH_3)_2O$	NH_2CH_2COOH?		PAHs
C_2 •	C_2S	C_3O	l-C_3H_2	CH_3CN •	HC_5N	C_7H	CH_3CH_2OH •	$HOCH_2CH_2OH$ •		C_{60}^+?
CH •	CH_2	C_3S	c-C_3H_2	CH_3NC	$HCOCH_3$	H_2C_6	HC_7N			
CH^+	HCN •	C_2H_2 •	CH_2CN	CH_3OH •	NH_2CH_3	$HOCH_2CHO$	C_8H			
CN •	HCO	CH_2D^+?	CH_4 •	CH_3SH	c-C_2H_4O		CH_2OHCHO •			
CO •	HCO^+	HCCN	HC_3N •	HC_3NH^+						
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO						
CP	HOC^+	HNCO •	HCOOH •	NH_2CHO •						
CSi	H_2O •	HNCS	H_2CHN	C_5N						
HCl	H_2S •	$HOCO^+$	H_2C_2O							
KCl	HNC •	H_2CO •	H_2NCN							
NH	HNO	H_2CN	HNC_3							
NO •	MgCN	H_2CS •	SiH_4							
NS	MgNC	H_3O^+ •	H_2COH^+							
NaCl	N_2H^+	NH_3 •								
OH •	N_2O	SiC_3								
PN	NaCN	CH_3								
SO •	OCS •									
SO^+	SO_2 •									
SiN	c-SiC_2									
SiO	CO_2 •									
SiS	NH_2 •									
CS •	H_3^+									
HF	H_2D^+									

• in comets

A Typical Interstellar Ice Absorption Spectrum as Measured by the ISO Satellite



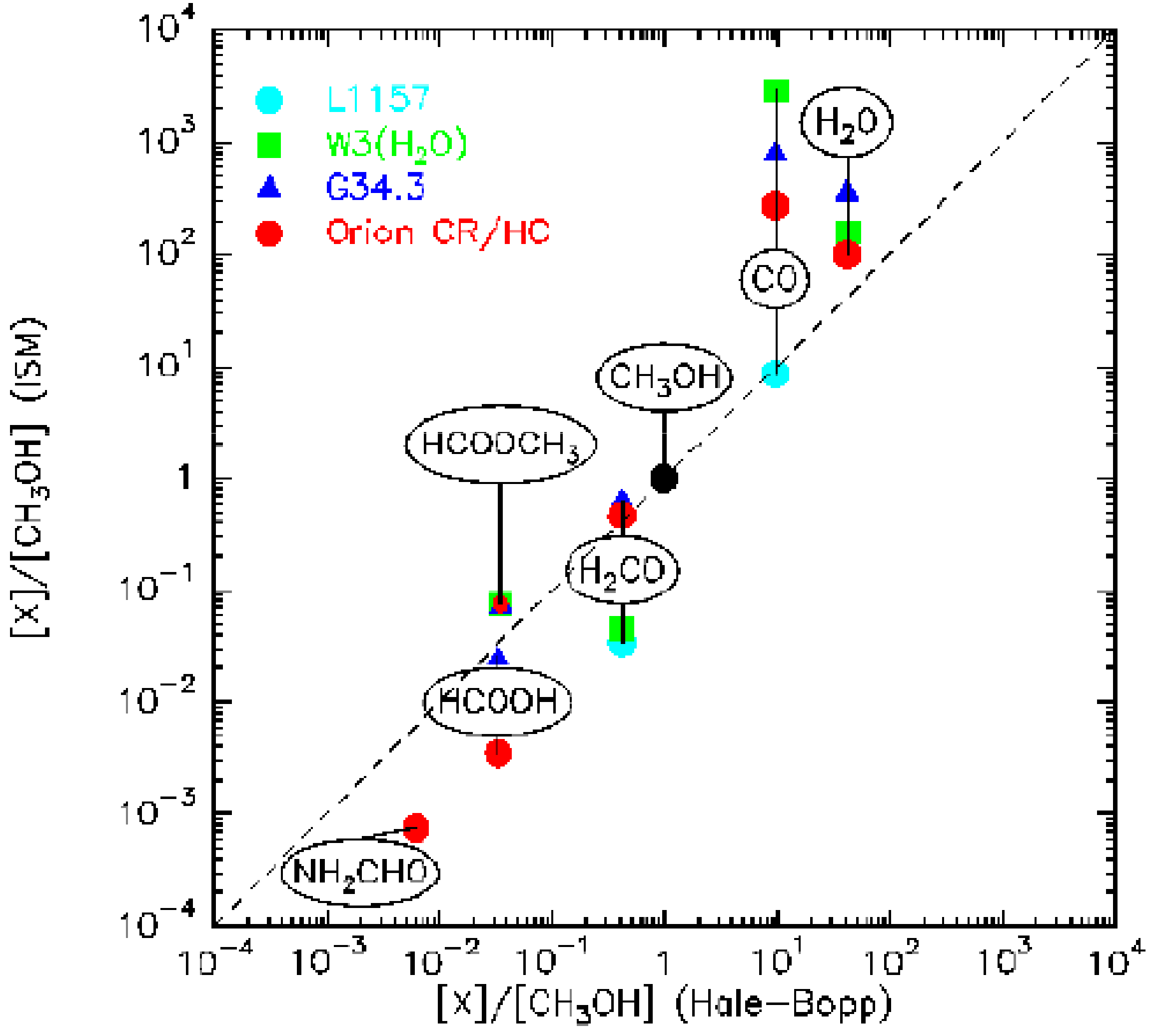
Courtesy Doug Hudgins

Ice Abundances in the ISM and in Comets

Species	Protostars	Comets
H_2O	100	100
CO	1-15 (polar)	5-20
	1-50 (apolar)	
CO_2	15-40	2-10
CH_4	1-4	0.2-1.2
CH_3OH	1-35	0.3-2
H_2CO	3	0.2-1
OCS	0.05-0.18	0.5
NH_3	3-10	0.6-1.8
C_2H_6	<0.4	0.4-1.2
HCOOH	3	0.05
N_2	?	?
OCN^-	0.3-2.9	-
HCN	<3	0.2

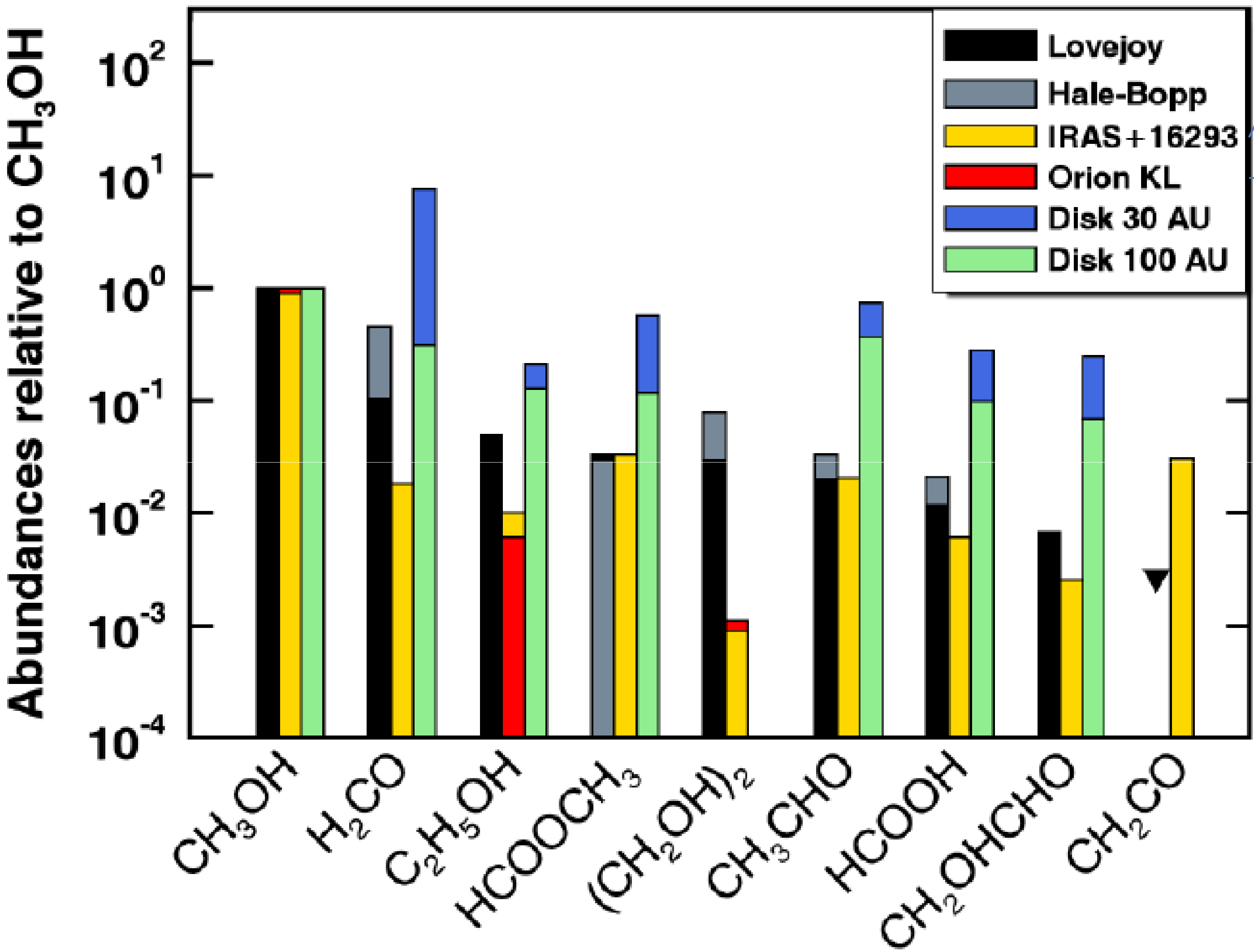
Courtesy Pascal Ehrenfreundt

Cometary molecules : the ISM connexion



Bockelée-Morvan et al. 2000

Cometary molecules : the ISM connexion



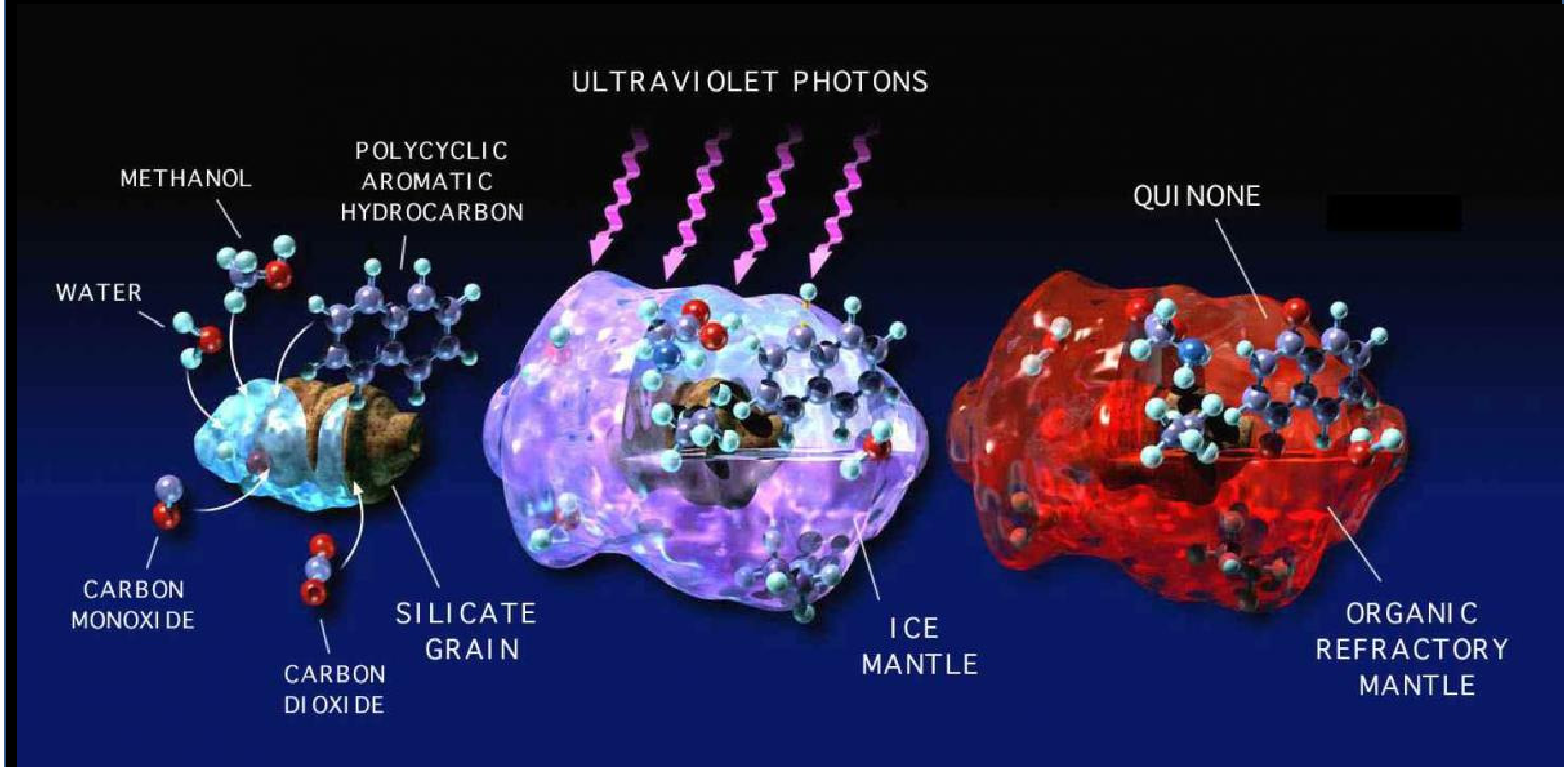
Jorgensen et al.
Bisshop et al.

Brouillet et al.

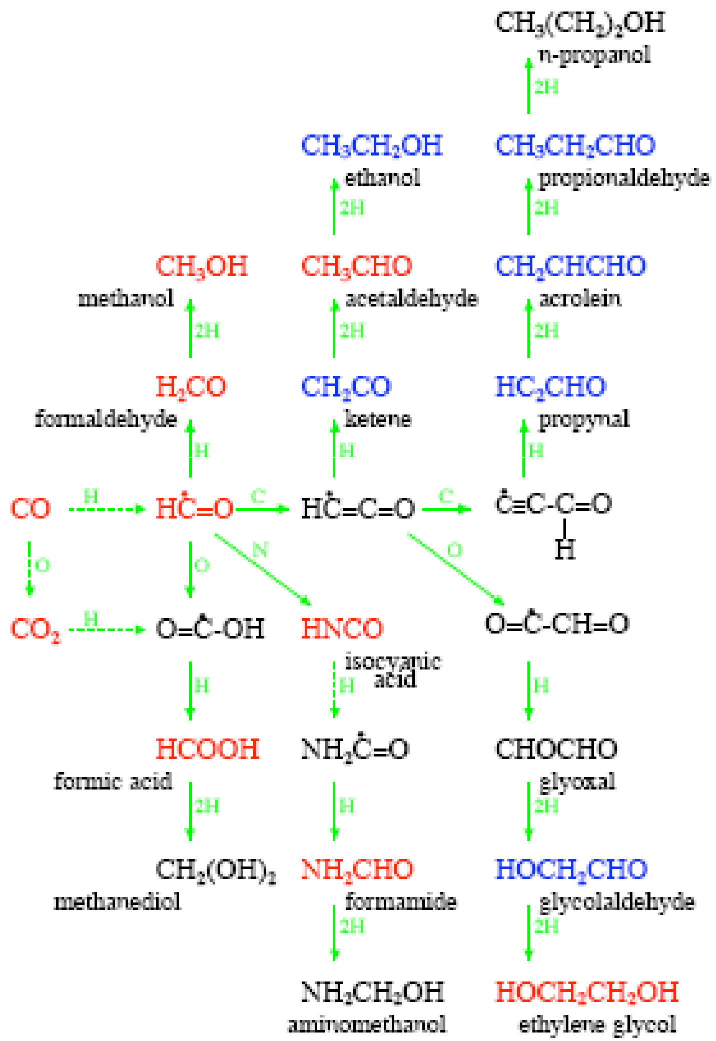
Walsh et al. 2014

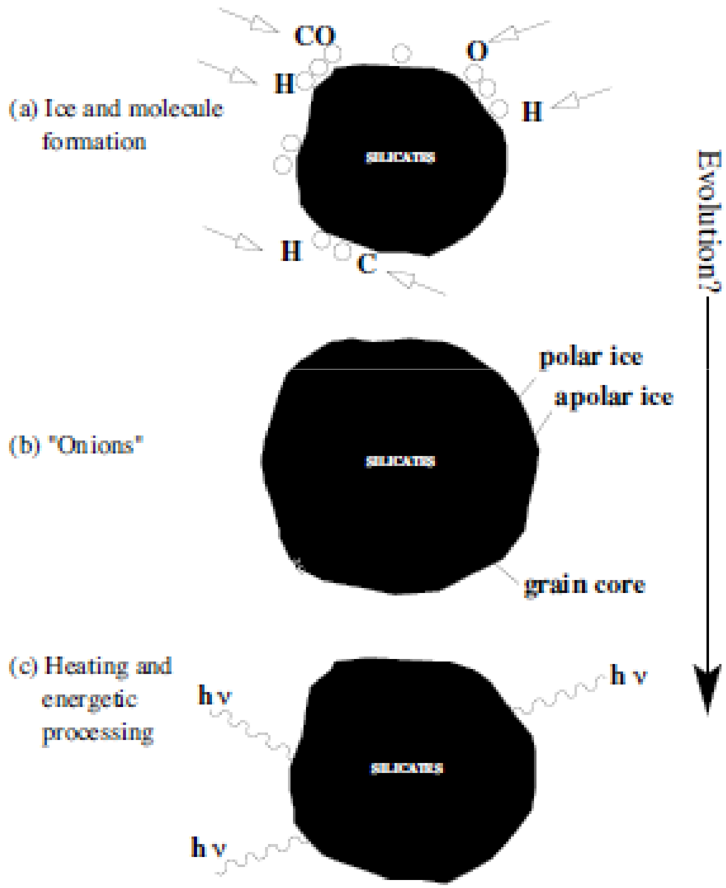
Biver et al. 2015

Synthesis of organic molecules



Grain surface reactions



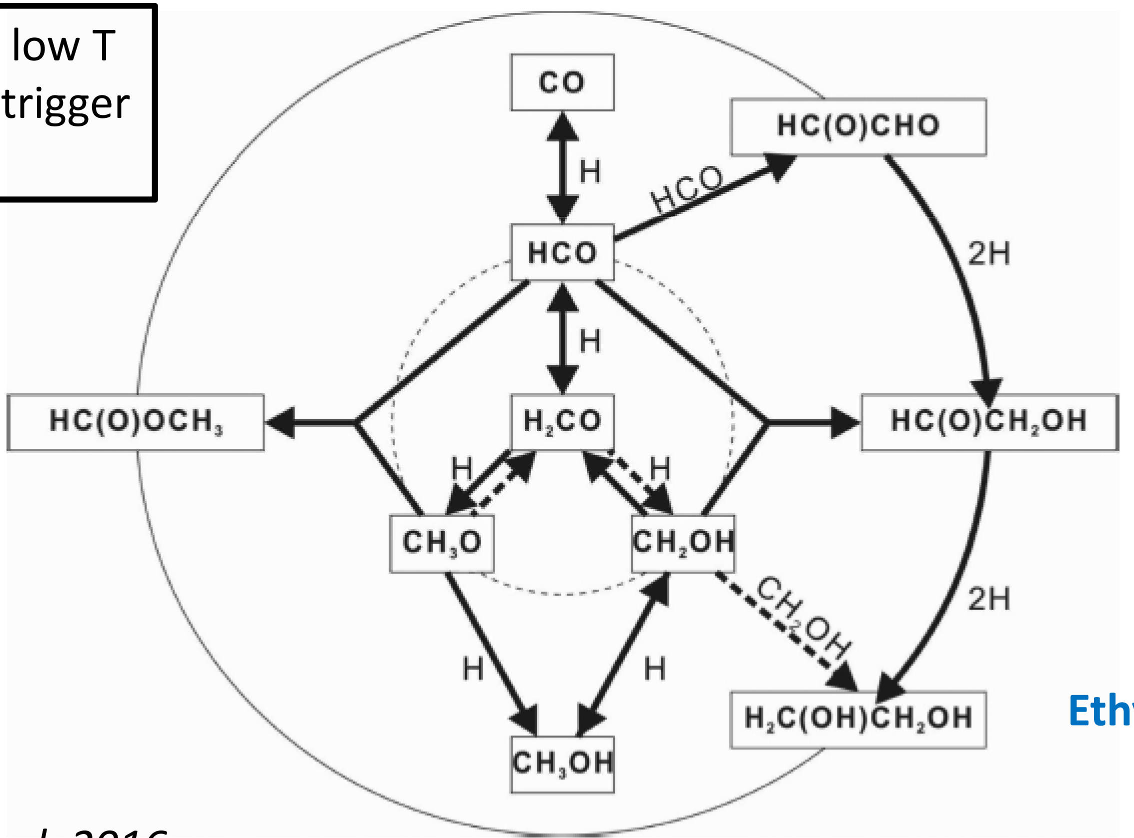


Charnley, 2008

Formation processes for cometary molecules

- Similarity between ISM and cometary ices → same formation pathways
- Laboratory experiments : direct evidence of complex species formation by H-atom addition, H-abstraction followed by radical recombination

Process occurs at low T without external trigger (e.g. UV)



Methyl formate

Glycolaldehyde

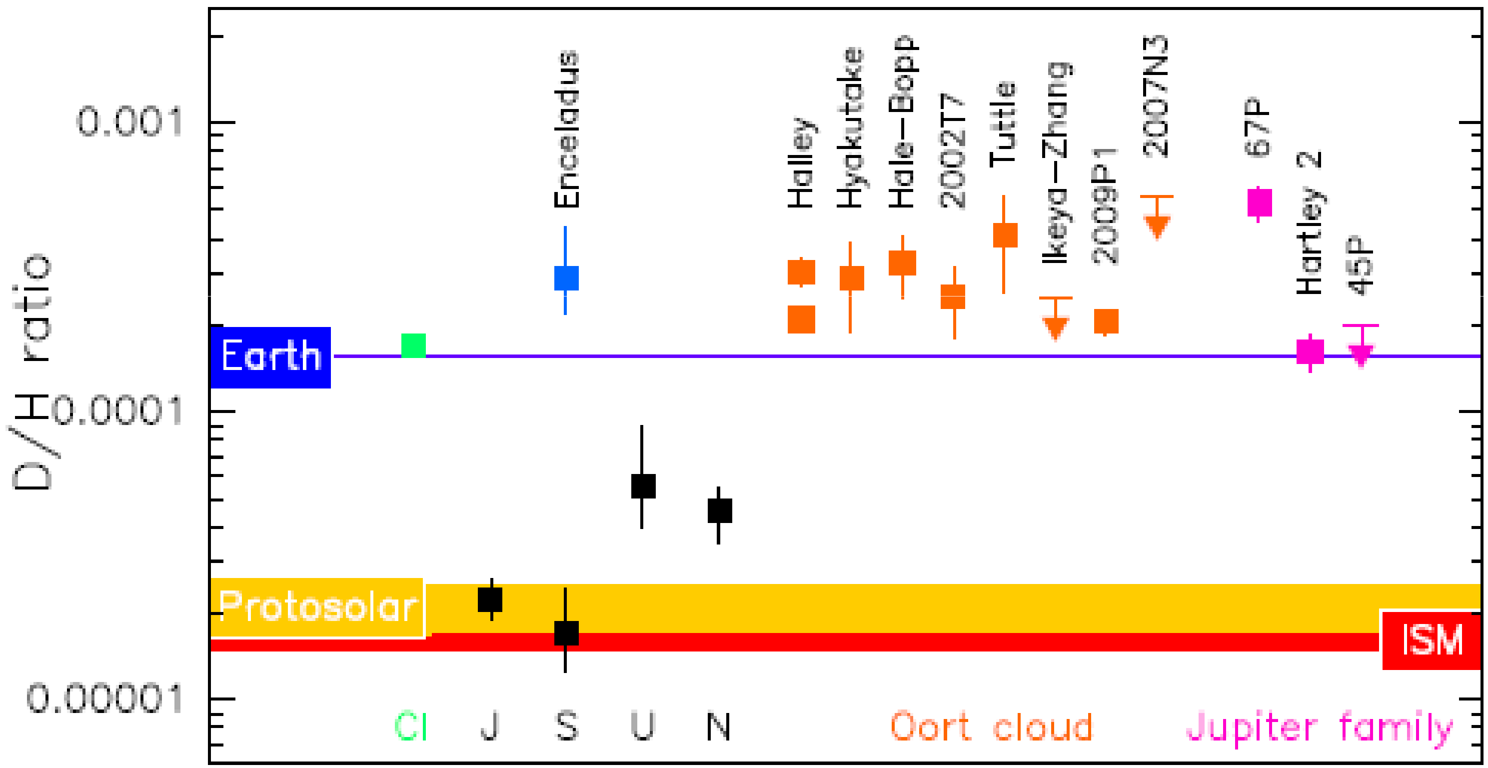
Ethylene glycol

Methanol

Chuang et al. 2016

Isotopic composition of cometary volatiles

D/H ratio in comets and the Solar System



Ocean-like water in the Jupiter-family comet 103P/Hartley 2

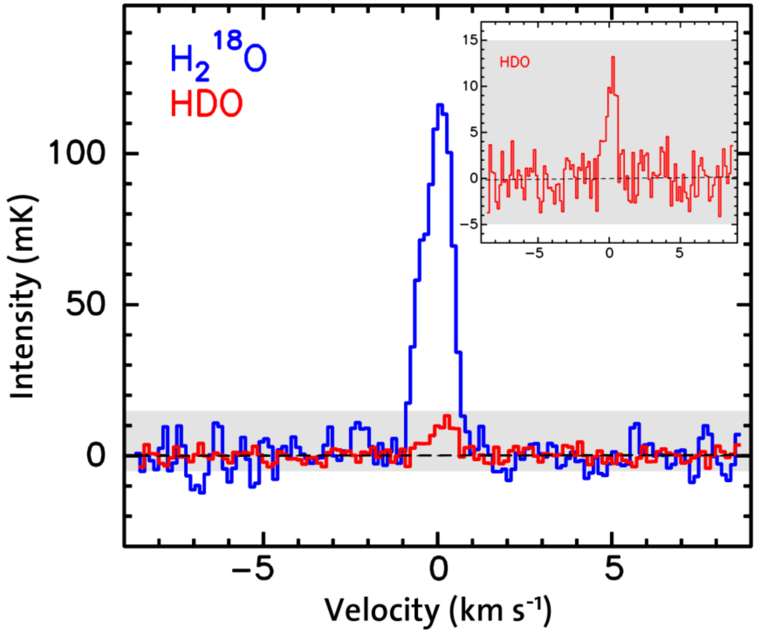
Paul Hartogh[1], Dariusz C. Lis[2], Dominique Bockelée-Morvan[3], Miguel de Val-Borro[1], Nicolas Biver[3], Michael Küppers[4], Martin Emprechtinger[2], Edwin A. Bergin[5], Jacques Crovisier[3], Miriam Rengel[1], Raphael Moreno[3], Slawomira Szutowicz[6] & Geoffrey A. Blake[2]

Published online 5 October 2011 | Nature |
doi:10.1038/news.2011.579

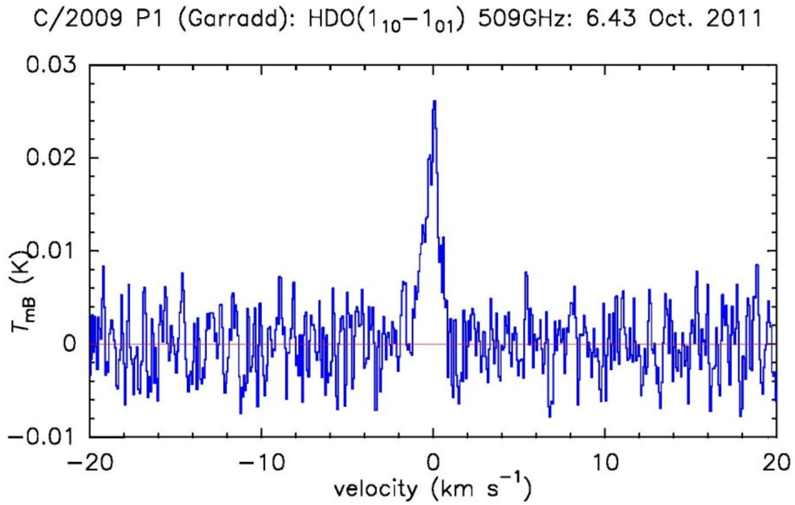
News

Comets take pole position as water bearers

Matching chemical signatures indicate that Kuiper comets brought water to Earth.



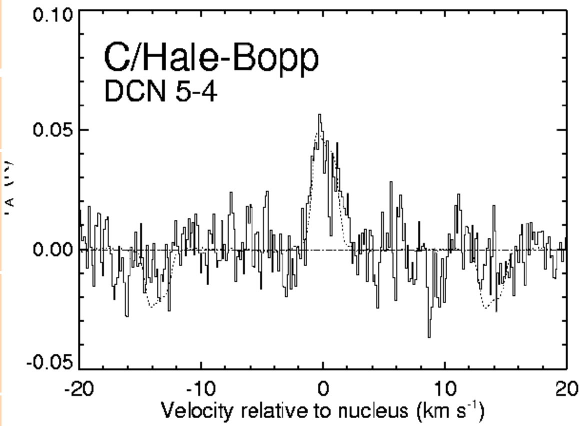
Detection of HDO in an Oort cloud comet



Bockelée-Morvan et al. 2012

D/H ratios in molecules other than water

	D/H		ISM
HCN	0.0023	Meier et al. 1998	0.01-0.1
NH_2D	< 0.04	Crovisier et al. 2004	
HDCO	< 0.05	Crovisier et al. 2004	0.035-0.15
CH_3OD	< 0.03	Crovisier et al. 2004	0.01-0.06
CH_2DOH	< 0.008	Crovisier et al. 2004	0.01
HDS	< 0.2	Crovisier et al. 2004	0.005-0.05
	<0.007	Biver et al. 2008	0.005-0.05
CH_3D	< 0.0025	Gibb et al. 2008	< 0.03
	< 0.006	Kawakita & Kobayashi 2008	
	< 0.005	Bonev et al. 2009	



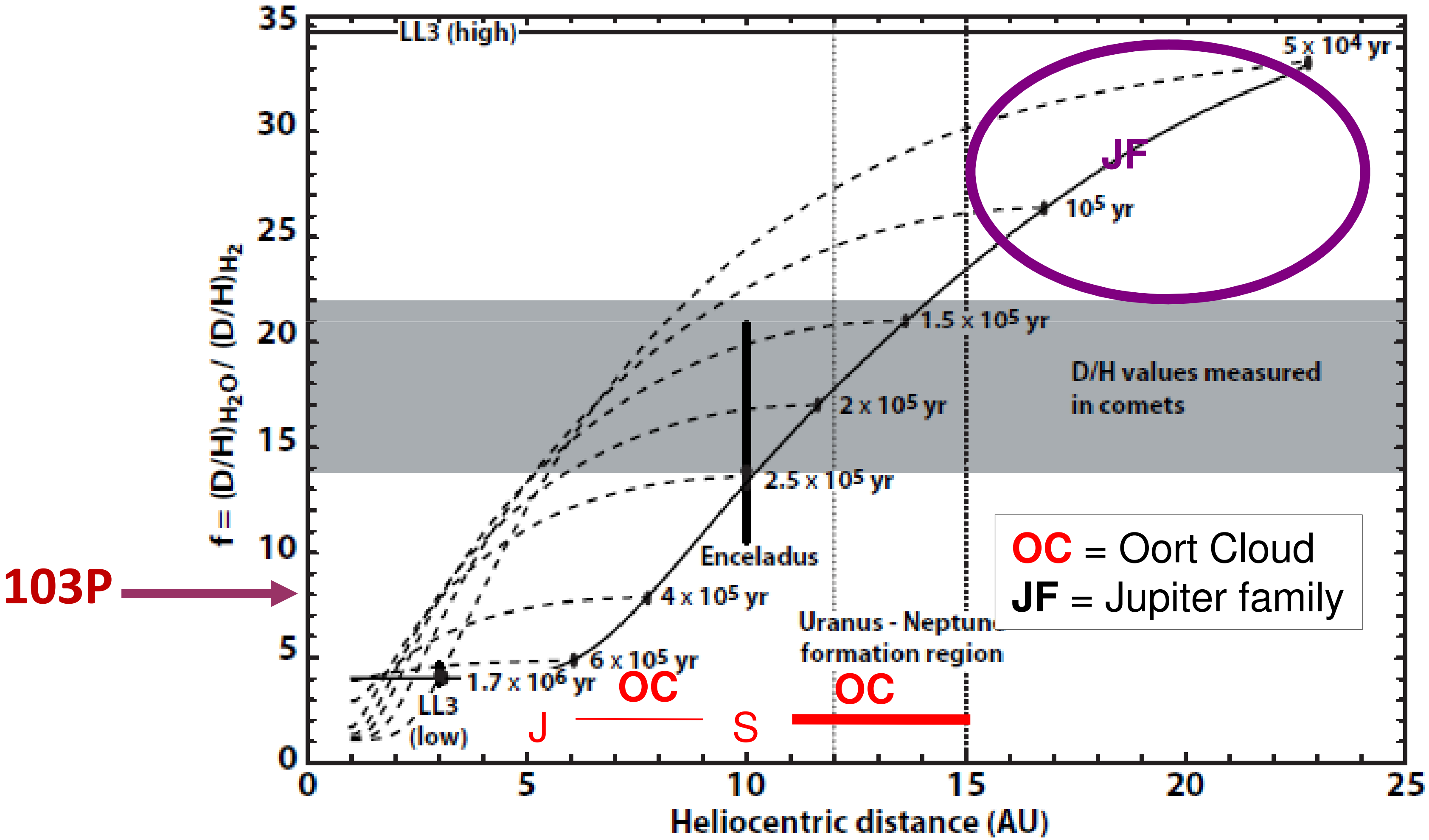
Meier et al. 1998

D_2O & HDS measured in 67P

- D/H in H_2S ~ 10^{-3}

Model Predictions for D/H in comets

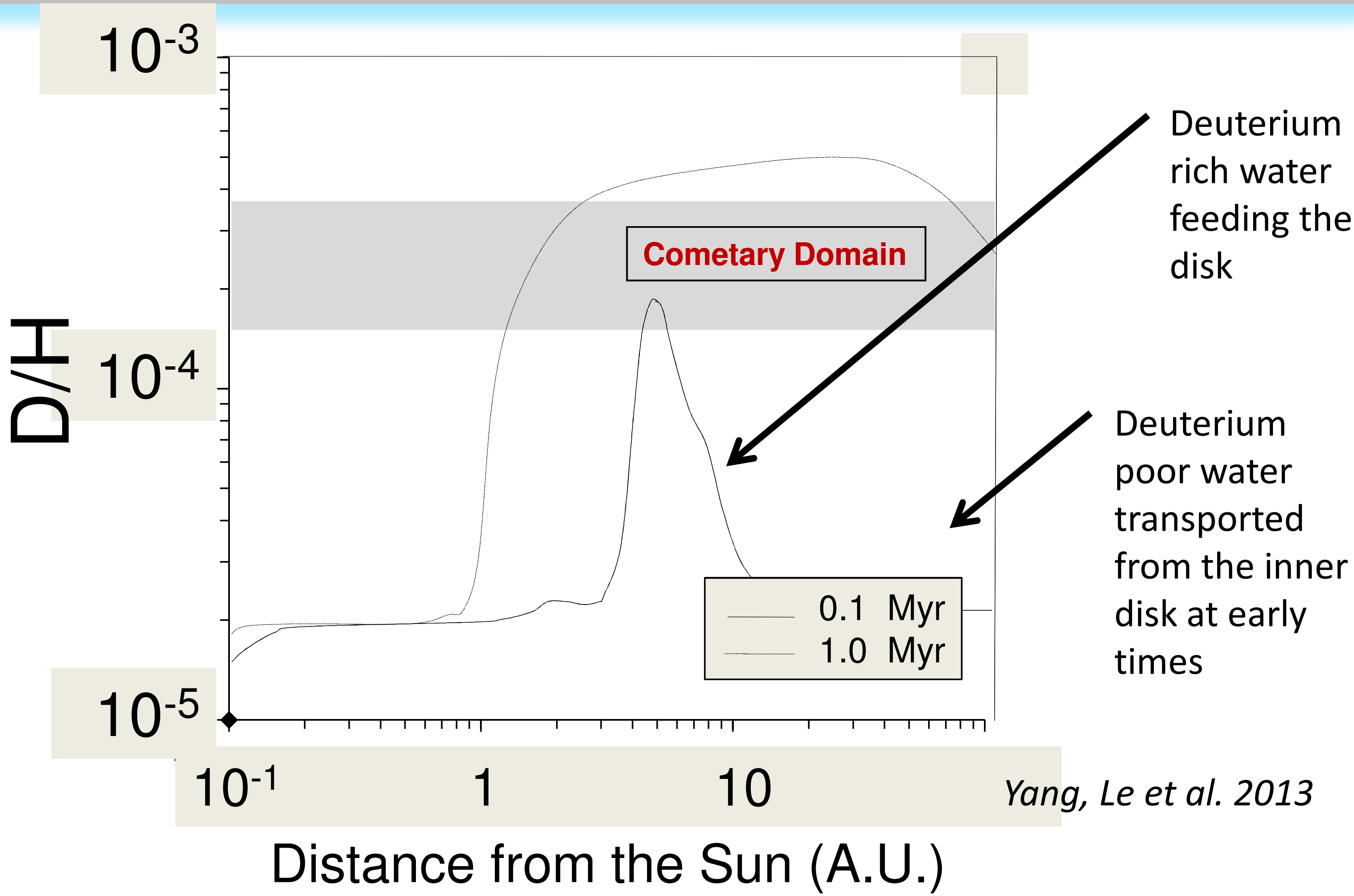
- isotopic exchange between H_2O and HD and turbulent mixing in an evolving Solar Nebula
- the Solar Nebula is here not anymore accreting mass from the presolar cloud



Takes into account planet migration

Kaveelars et al. (2011)

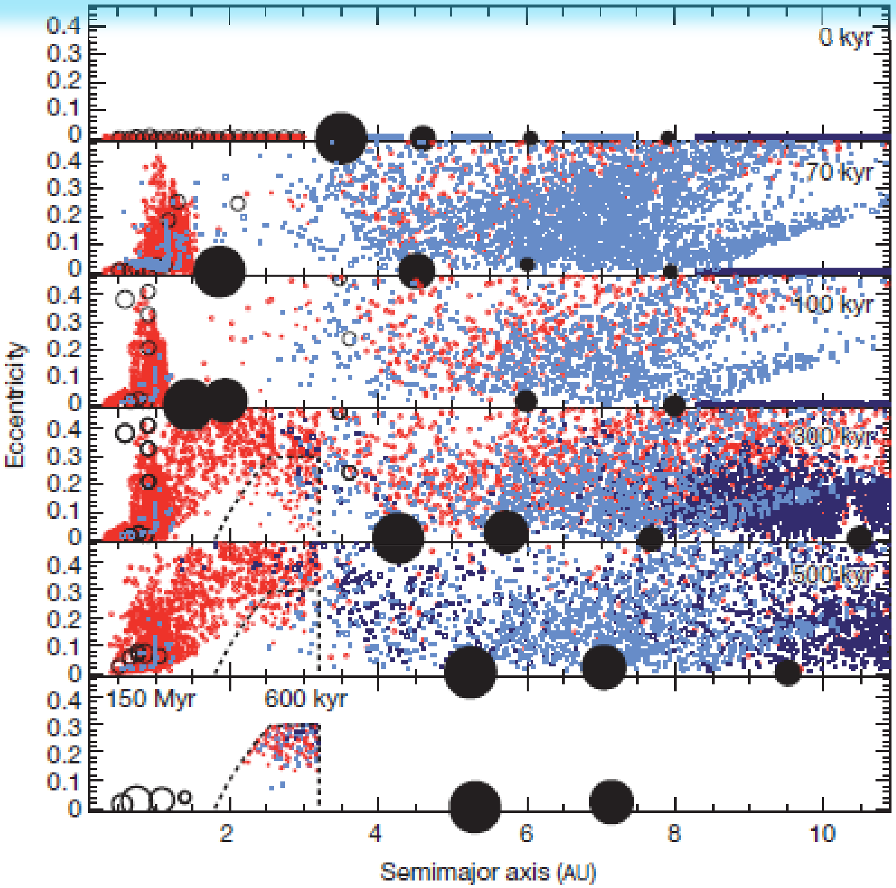
Model Predictions for D/H in comets

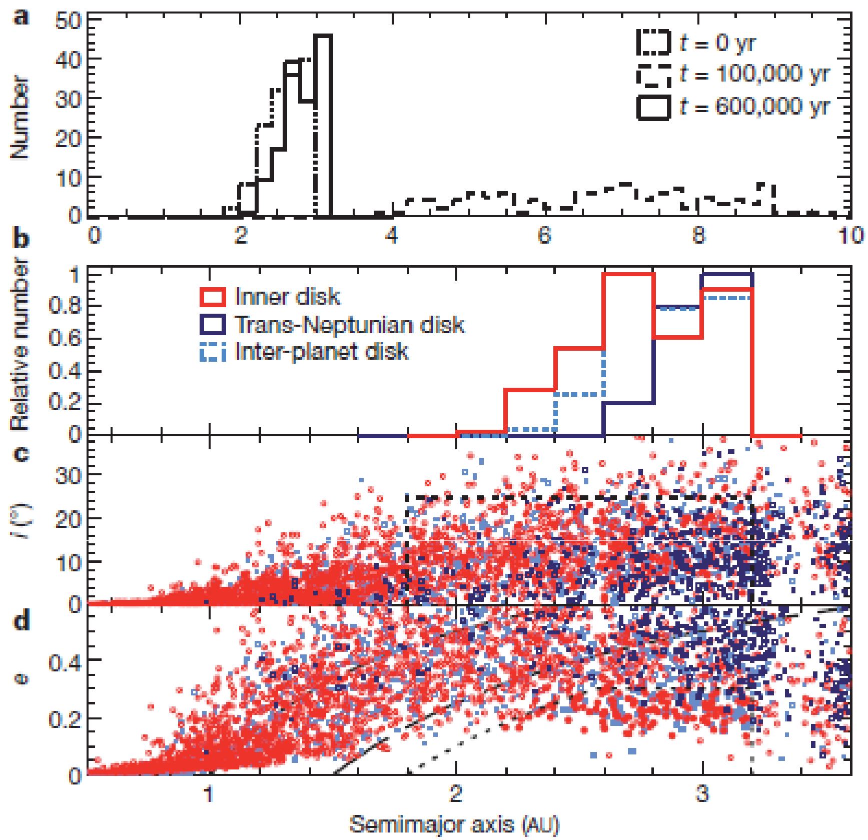


Yang, Le et al. 2013

Unlike previous models, the solar nebula is continuously accreting D/H-enriched material

Diversity is consistent with radial mixing of planesimals – Grand Tack model

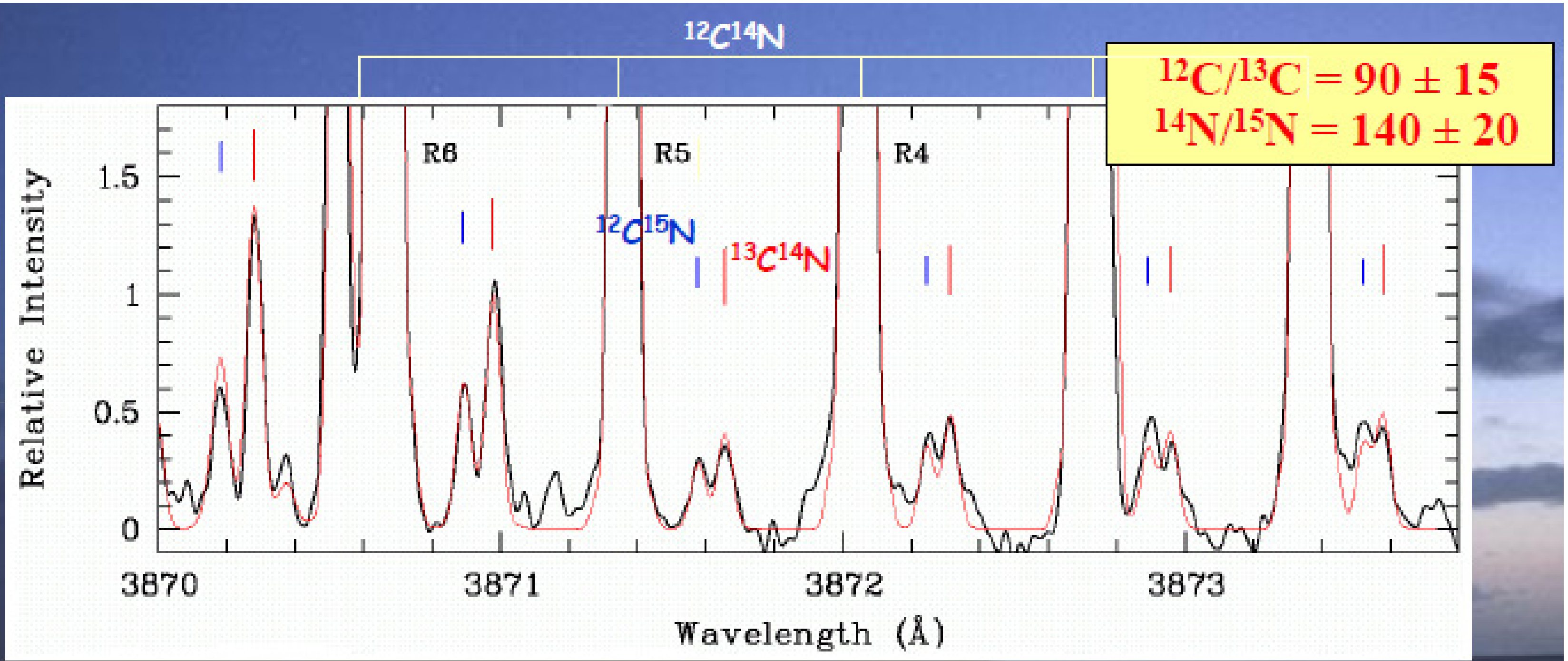




Walsh et al., Nature Juin 2011

- **Grand Tack**: inward then outward migration of Jupiter and Saturn
- Type 2 ''inward migration'' in gaseous nebula
- Explain Mars mass and distribution of S/C/D asteroids in the main belt
- TNOs on eccentric Earth-crossing orbits

Isotopic ratios from UV or Visible spectroscopy



A section of the UVES spectrum of the CN (0,0) violet band in comet 88P/Howell (m_r ~ 8.0).

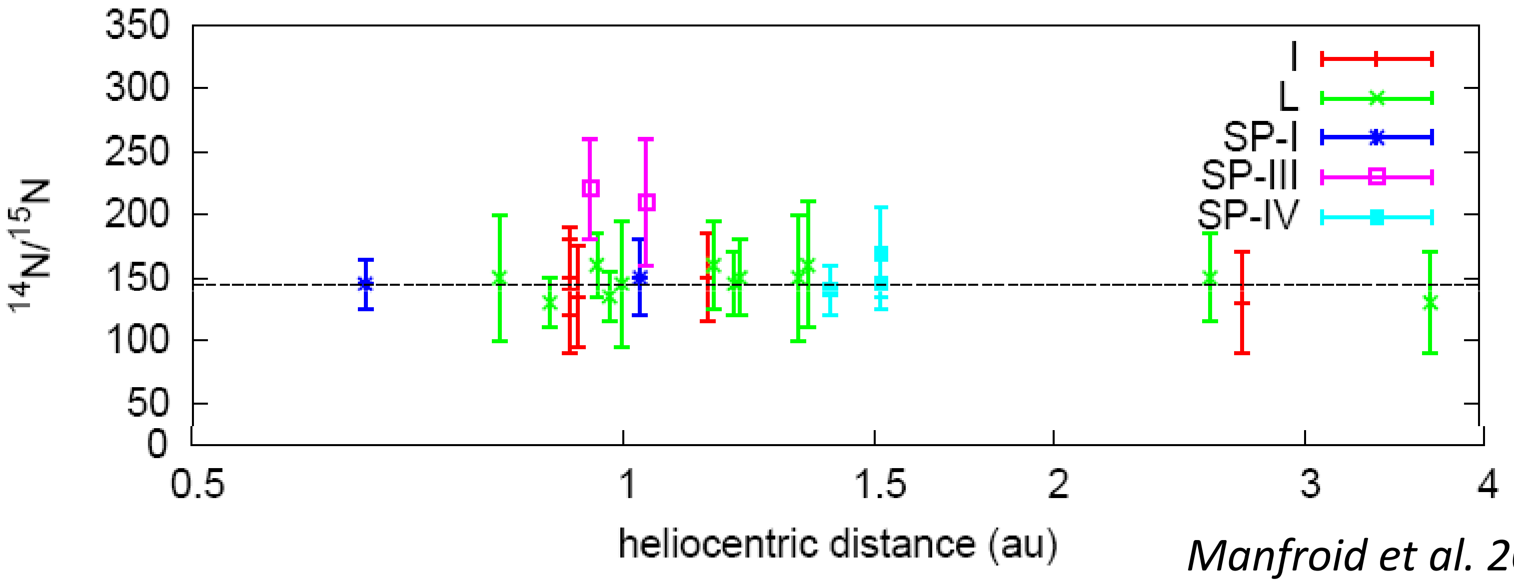
Thick (black) line: mean observed spectrum (**total of 12 hrs exptime**);
Thin (red) line: synthetic spectrum of $^{12}C^{14}N$, $^{12}C^{15}N$ and $^{13}C^{14}N$ with the adopted isotopic abundances. The lines of $^{12}C^{15}N$ are identified by the *short ticks* and those of $^{13}C^{14}N$ by the *tall ticks*. The quantum numbers of the R lines of $^{12}C^{14}N$ are also indicated.

Hutsemékers et al. A&A 2005

Isotopic ratios in volatiles : nitrogen

Measurements in CN from UV spectroscopy

(different colors correspond to different dynamical classes and Tisserand parameter)

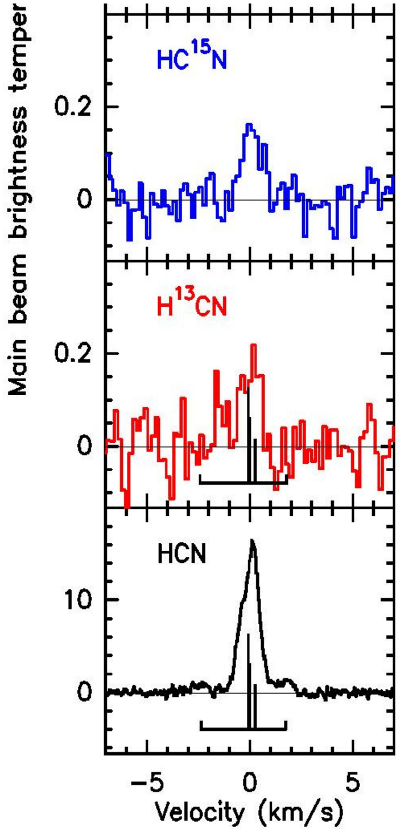


Manfroid et al. 2009

- Isotopic anomalies in the $^{14}N/^{15}N$ ratio : enrichment by a factor of 2 in ^{15}N wrt the terrestrial value (=272) measured in 18 comets **(mean = 148+/-6)**
- $^{14}N/^{15}N$ identical in JFCs and OCCs, but one comet (73P) is less ^{15}N-enriched
- no variation with heliocentric distance: if there are several sources of CN, they share the same isotopic ratio

Isotopic ratios in volatiles: nitrogen

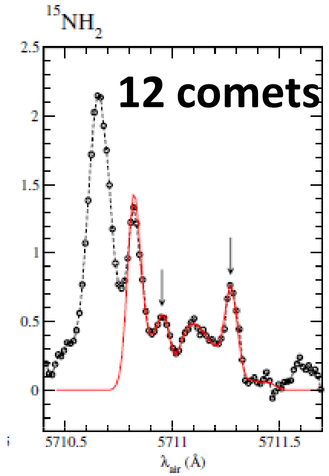
Measurements in HCN

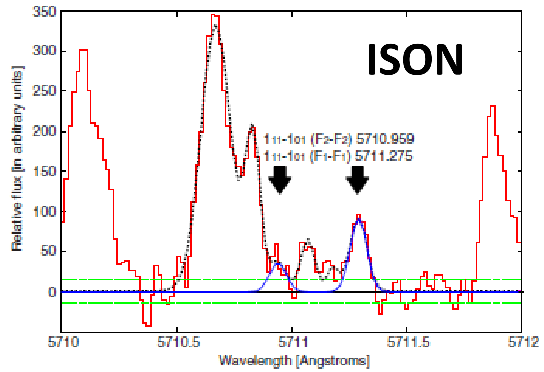


Bockelée-Morvan et al. 2008

- **17P/Holmes**
  $^{14}N/^{15}N$ = 139 ± 26
- consistent with value in CN

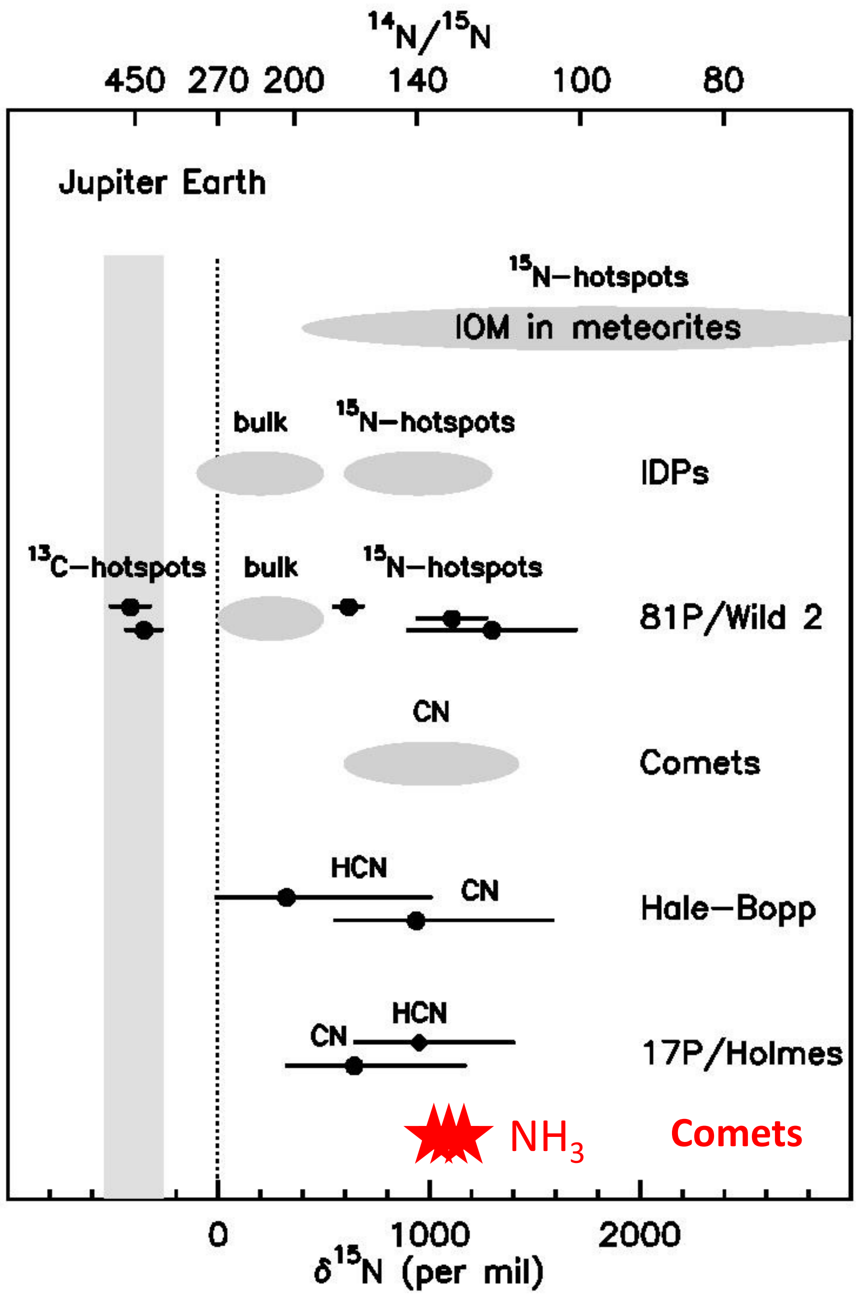
Measurements in NH_3 from NH_2





- **12 comets**
  $^{14}N/^{15}N$ = 130 (Rousselot et al. 2014)
- **C/2012 S1 (ISON)**
  $^{14}N/^{15}N$ = 139 ± 38 (Shinnaka et al. 2014)
- **C/2012 F6 (Lemmon)**
  $^{14}N/^{15}N$ = 137 ± 45 (Decock et al. This conf)

- HCN and other major parents of CN are equally enriched in ^{15}N
- Same ^{15}N enrichment in HCN and NH_3



$^{14}N/^{15}N$
450 270 200 140 100 80
Jupiter Earth
^{15}N–hotspots
IOM in meteorites
bulk
^{15}N–hotspots
IDPs
^{13}C–hotspots
bulk
^{15}N–hotspots
81P/Wild 2
CN
Comets
HCN
CN
Hale–Bopp
HCN
CN
17P/Holmes
NH_3
Comets
0 1000 2000
$\delta^{15}N$ (per mil)

Interpretations of ^{15}N enrichment

- **In proto-stellar sources :** dichotomy between CN-bearing (^{15}N-rich) and NH_3 (no fract.)

- **Gas-phase chemical models of the ISM** : two pathways for ^{15}N fractionation (Rodgers & Charnley , 2008)
  - to N_2 and NH_3 (slow: 10^6 yr)
  - from N to HCN and other nitriles (rapid: 10^5 yr)

✓ consistent with ISM sources

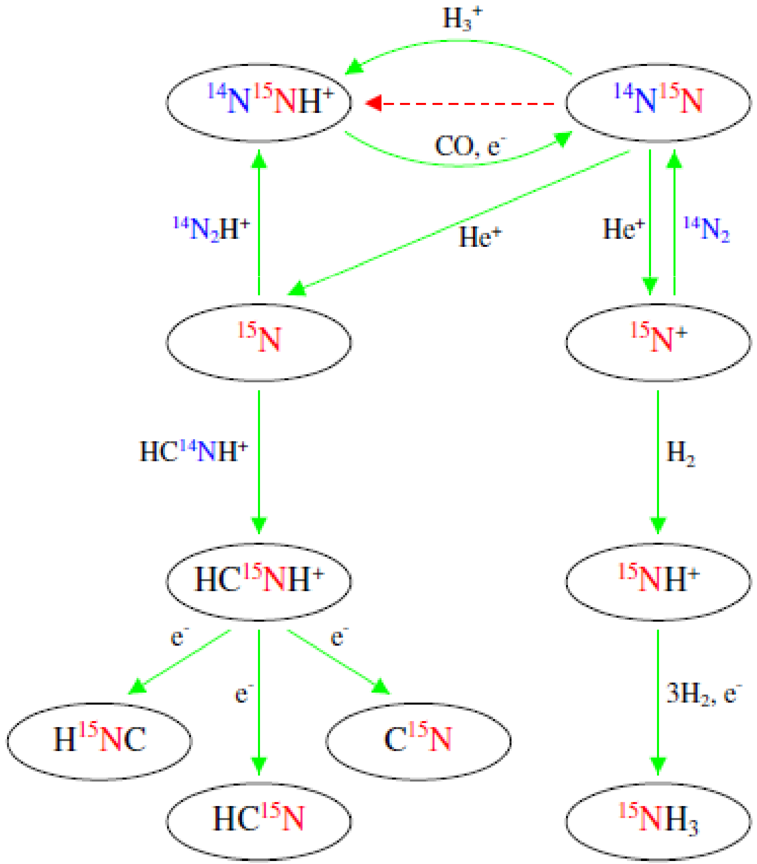
✓ comet material : longer time scales ?

- **Grain-surface chemistry :**
  formation of ammonia from ^{15}N-rich atomic N ?

- **Models considering self-shielding of N_2 photodissociation** (Heays et al. 2014)

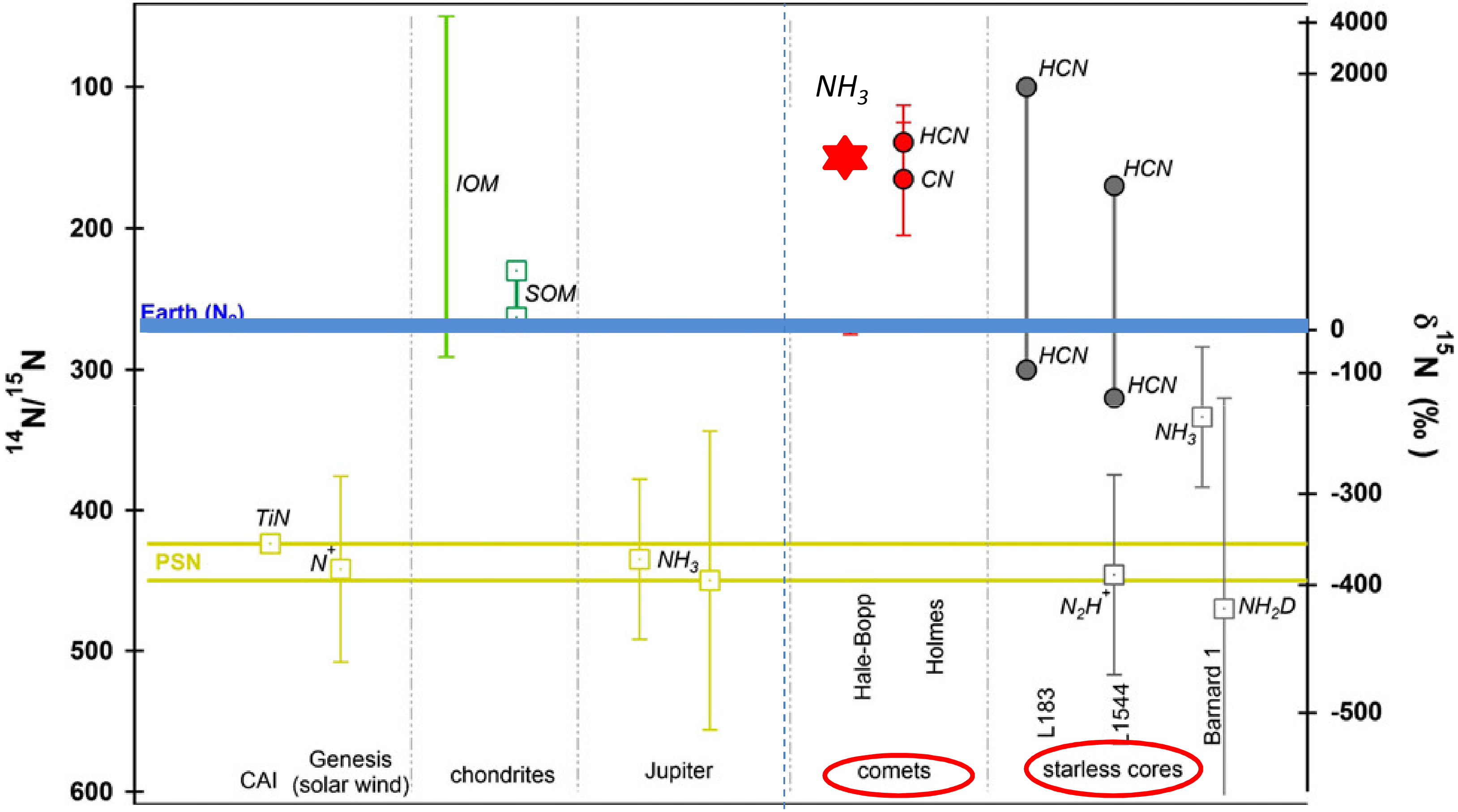
✓ explain ^{15}N enrichment in HCN

✓ less clear for NH_3



Wirstrom et al. (2012)

Comparison with prestellar cores



Hily-Brandt et al. 2013

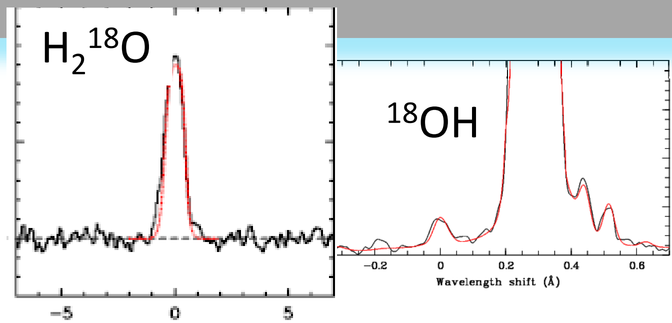
Table 1. Interstellar Nitrogen Isotope Ratios

Source	Type	NH_3	$N_2H^{+\S}$	HCN	HNC	CN	Ref.
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	>297	...	...	...	3,3
			175±79				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	$300\pm^{55}_{40}$	>600	$165\pm^{30}_{25}$	$75\pm^{25}_{15}$	240	10,10,10,10,9
		334±50	$400\pm^{100}_{65}$				6,10
		$470\pm^{170}_{100}$					4
L1689N	Class 0 protostar	$810\pm^{600}_{250}$	...	...	...	...	4
Cha-MMS1	Class 0 protostar	...	$729\pm^{212}_{135}$	...	135	...	16,7
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	>410	...	...	...	3,3
			>410				3
Several	Massive starless cores	...	65-1100	...	...	330-400	15,15
			180-1445#				15
Several	Massive protostars	...	190-1000	...	...	190-450	15,15
			180-1300				15
Several	UC HII regions	...	320-900	...	...	230-430	15,15
			350-700				15
Comets	JFC & Oort Cloud	127‡	...	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. (2015); (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); (11) Rousselot et al. (2014); (12) Bockelée-Morvan et al. (2008); (13) Wampfler et al. (2014); (15) Fontani et al. (2015); (16) Cordiner et al., private communication.

Wirstrom et al 2016

Isotopic ratios in volatiles : oxygen



$^{16}O/^{18}O$ in H_2O only

Only a few measurements available :

- **From the Giotto NMS** in 1P/Halley : **518 ± 45, 470 ± 40** *(Balsiger et al. 1995, Eberhardt et al. 1995)*
- Detection of $H_2^{18}O$ in the submillimeter in 4 comets *(Biver et al. 2007)* using the Odin satellite **530 ± 60, 530 ± 70, 550 ± 75, 508 ± 33**
- **Measurements with Herschel in C/2009P1 : 523 ± 32** *(Bockelée-Morvan et al. 2012)*
- *Rosina/Rosetta in comet 67P: terrestrial (Altwegg et al. 2015)*

Values consistent or slightly higher than the terrestrial value (=499)

- **Detection of ^{18}OH in the UV at VLT**

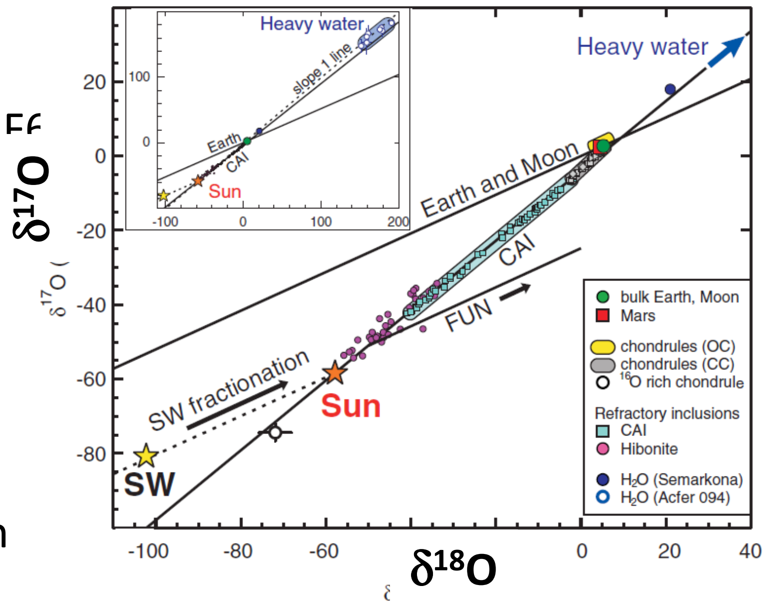
$^{16}O/^{18}O$ = **425 ± 55** in C/2002 T7, **300 ± 150** in C/2012 F6 *(Hutsemekers et al. 2008, Decock, this conf)*

Here, slightly lower than the Earth value

- ^{18}O excess consistent with self-shielding models (Yurimoto& Kuramoto 2004)

isotopic anomalies in H_2O due to selective dissociation

McKeegan et al. 2011



Summary

- Remote sensing spectroscopy provided important results concerning comet composition

- **≥ 20 molecules can be routinely detected** in bright comets (> 10^{29} mol/s)
- Sensitivity allows **isotopic ratios** to be measured
- **Origin of chemical diversity still elusive** but seems to be in part primordial
- **Major steps done by the Rosetta mission** : measurements still under analyses
- **New identifications also expected** with available or next-generation instrumentation (especially if extraordinarily bright comets are passing)

- **Comet ice composition shows strong similarities with interstellar clouds**
- Differences exists, e.g., regarding isotopic ratios D/H, $^{14}N/^{15}N$
- Cometary molecules formed in very cold environments, likely in the presolar cloud
- However comets contain also material formed in the solar nebula, even close to the star