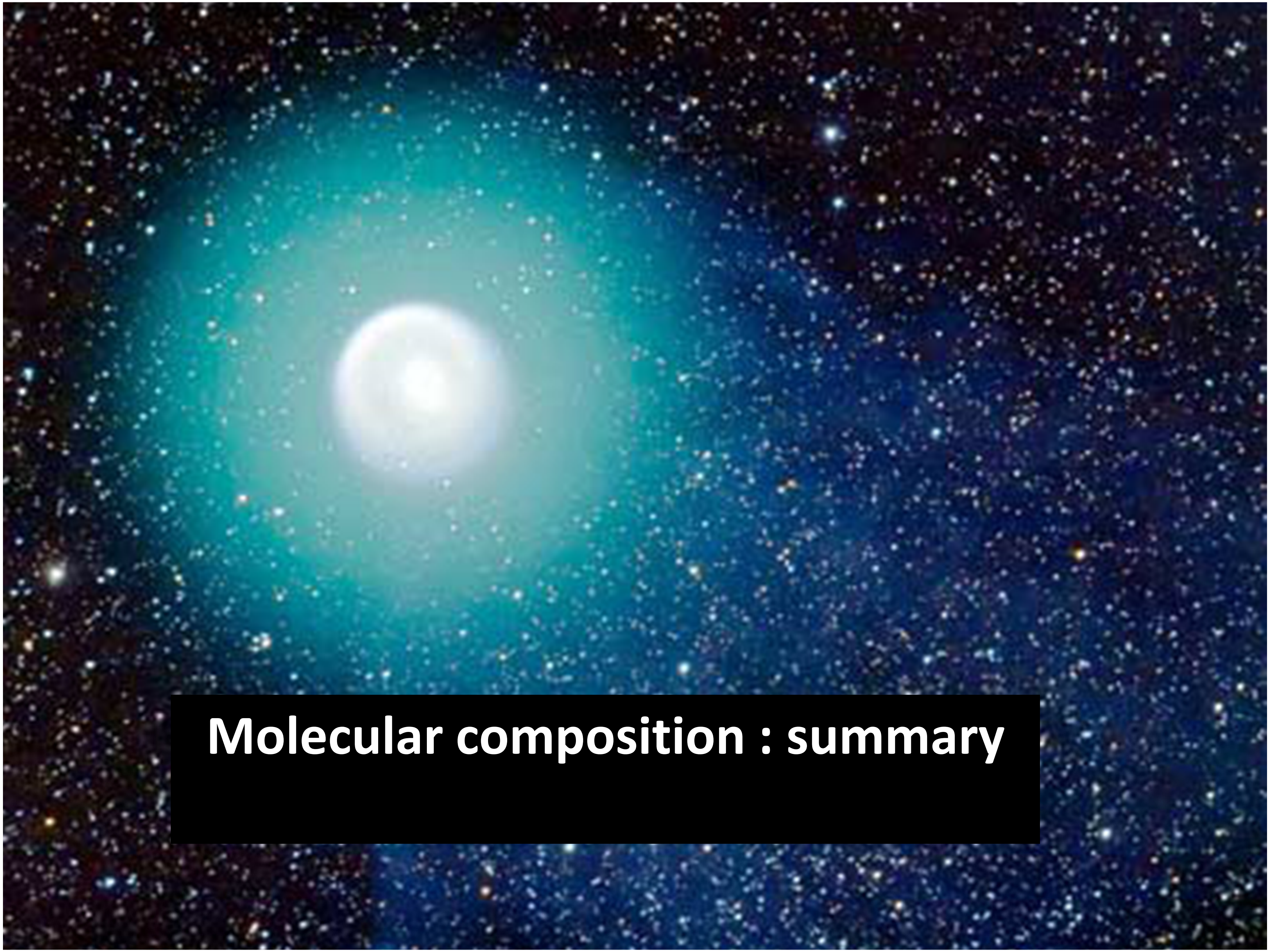
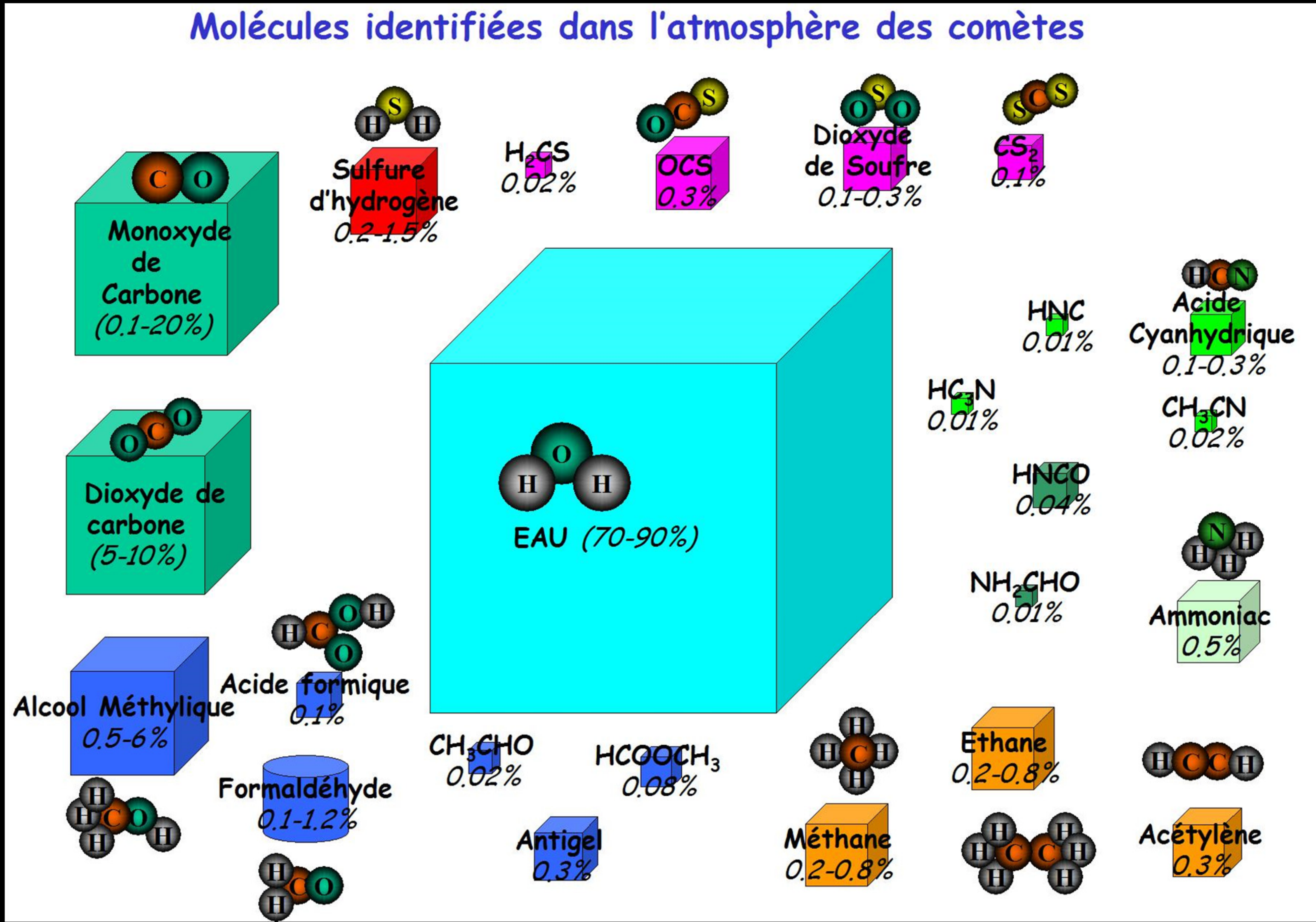
The molecular composition of comets

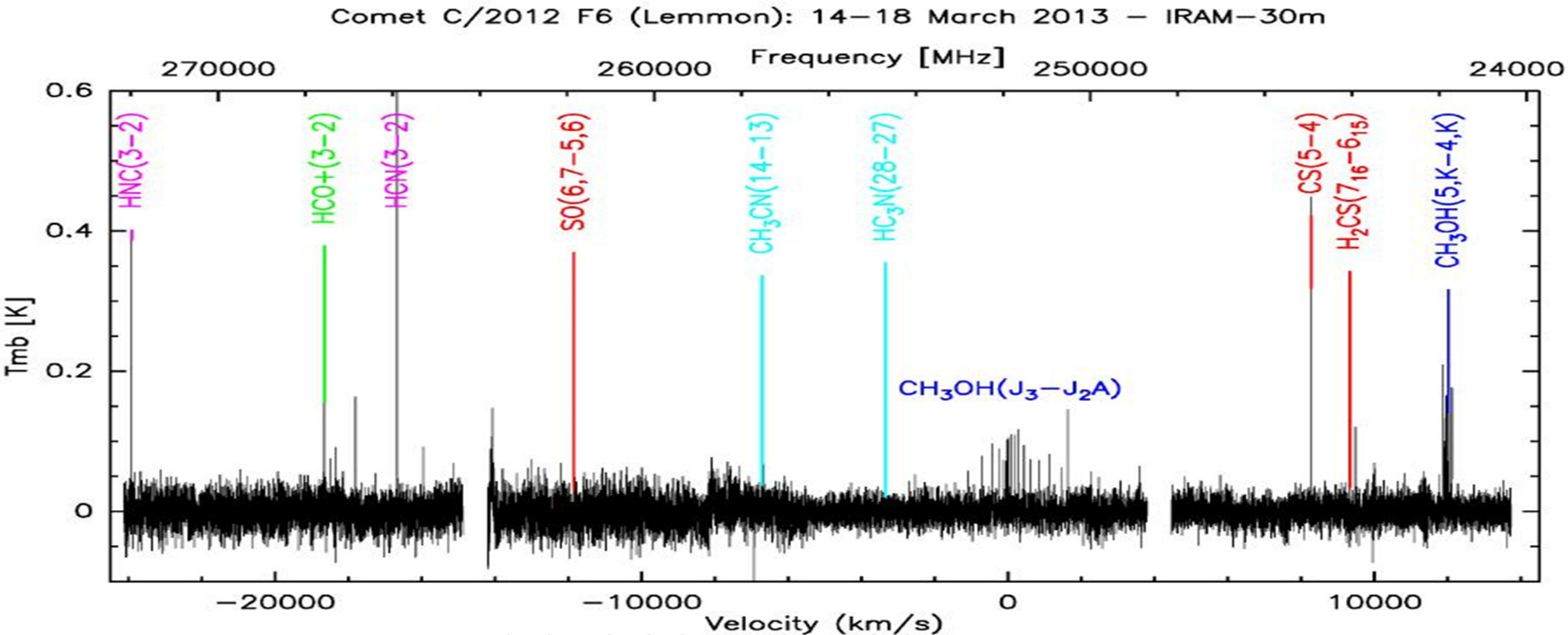
Dominique Bockelée-Morvan

Most Rosetta results concerning chemistry are embargoed !

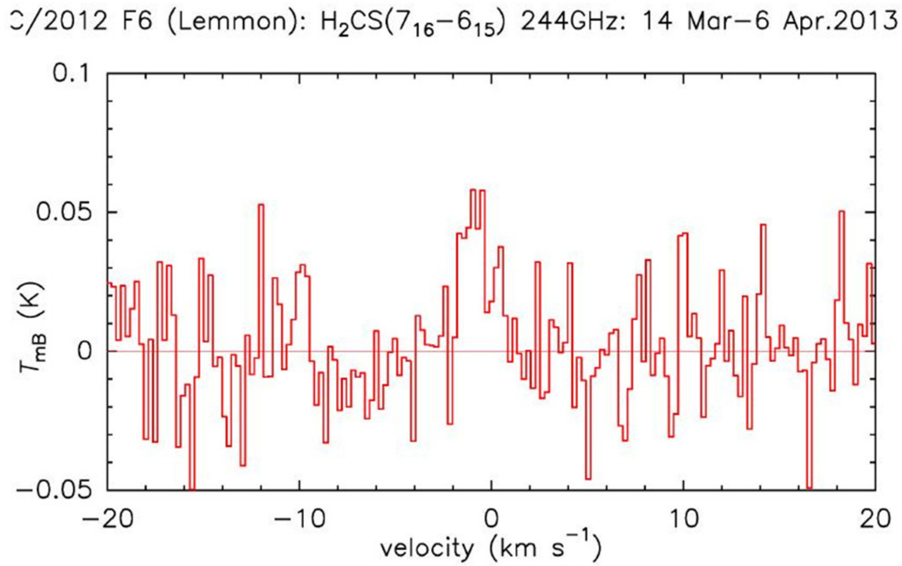

Molecular composition : summary

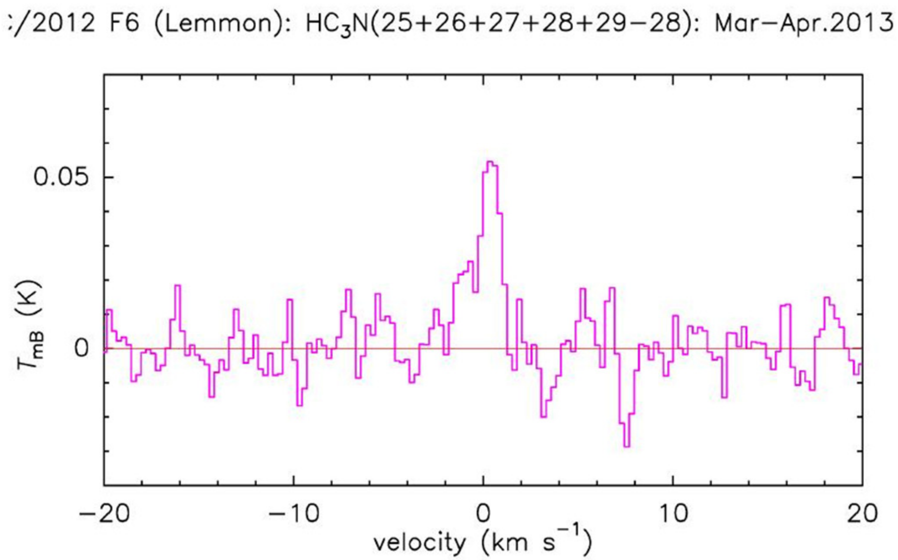
Composition des comètes : volatiles



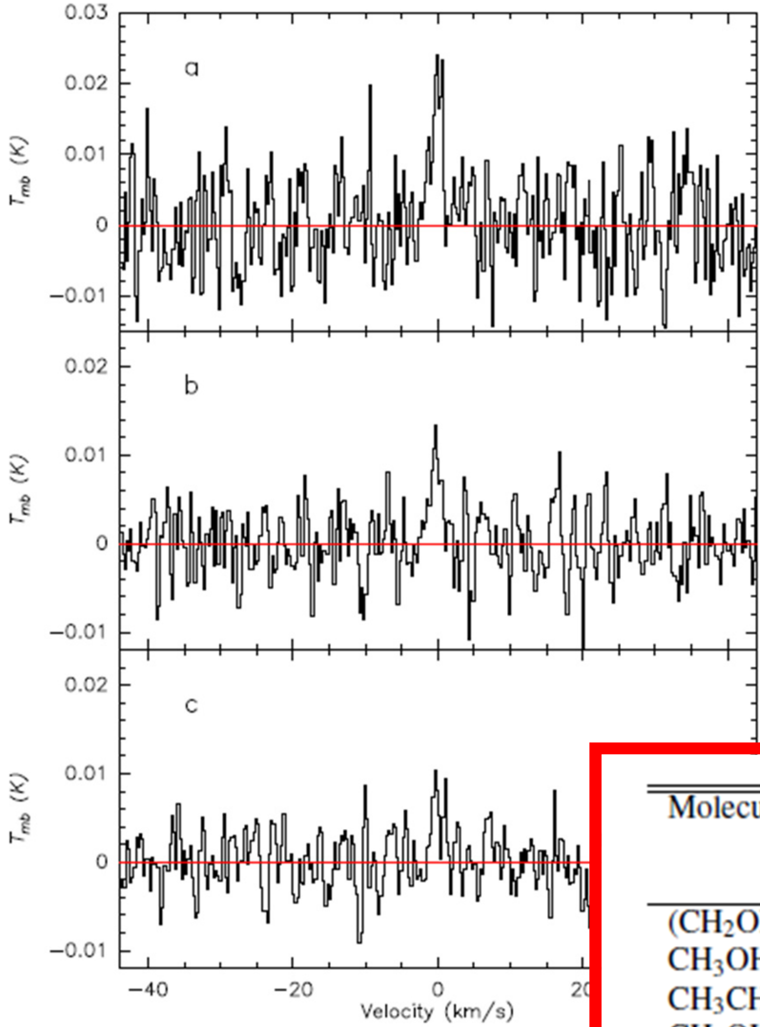


Frequency survey: 210-> 272 GHz, 166-170 GHz





Ethylene glycol and other CHO-bearing in comets Lovejoy and Lemmon



Biver et al. 2014

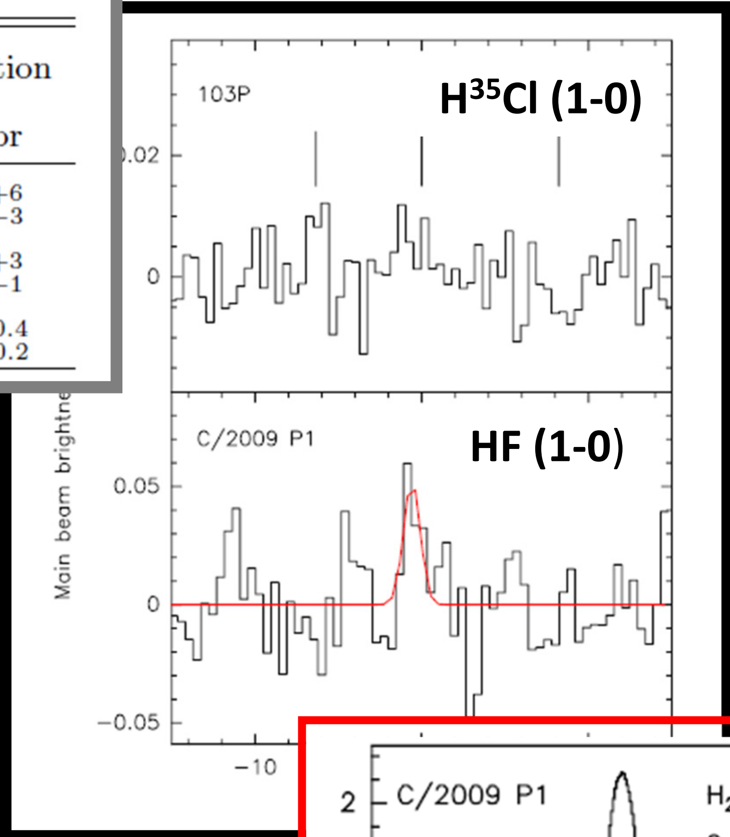
Molecule	Abundance (%) C/1995 O1[a] (Hale-Bopp)	C/2012 F6 (Lemmon)	C/2013 R1 (Lovejoy)
HCN	0.25	0.14	0.16
CO	23	4.0[b]	7.2[c]
H_2CO	1.1	0.7[c]	0.7[c]
CH_3OH	2.4	1.6	2.6
HCOOH	0.09	< 0.07	0.12
$(CH_2OH)_2$	0.25	0.24	0.35
HNCO	0.10	0.025[c]	0.021[c]
NH_2CHO	0.02	0.016	0.021
$HCOOCH_3$	0.08	< 0.16	< 0.20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

Brouillet et al. 2014

Molecule	Column density[a] (cm^{-2}) Orion-KL	Sgr B2	NGC 7129	Abondance ($\%H_2O$) Hale-Bopp	Lemmon	Lovejoy
$(CH_2OH)_2$	$4.6\ 10^{15}$	$2.3\ 10^{15}$	$2.0\ 10^{15}$	0.25	0.24	0.35
CH_3OH	$4.2\ 10^{18}$	$5.6\ 10^{18}$	$3.4\ 10^{20}$	2.4	1.6	2.6
CH_3CH_2OH	$2.5\ 10^{16}$	$2.1\ 10^{16}$	$3.0\ 10^{18}$	≤0.1	≤0.11	≤0.14
CH_2OHCHO	$\leq 3.5\ 10^{14}$	$1.8\ 10^{15}$	$1.0\ 10^{15}$	≤0.04	≤0.08	≤0.07

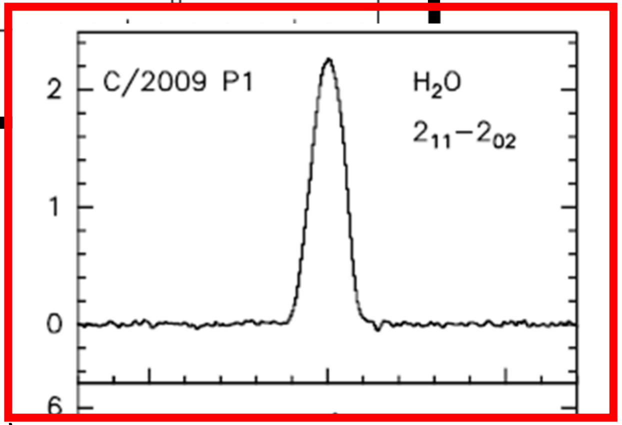
Search for HF and HCl with Herschel

HX	Comet	$Q(HX)/Q(H_2O)^a$ ($\times 10^{-4}$)	$(X/O)_\odot{}^b$ ($\times 10^{-4}$)	Depletion factor
HCl	103P	$< 1.1^c$	$6.5^{+6.4}_{-3.2}$	$> 6^{+6}_{-3}$
HCl	C/2009 P1	$< 2.2^d$	$6.5^{+6.4}_{-3.2}$	$> 3^{+3}_{-1}$
HF	C/2009 P1	$1.8{\pm}0.5^e$	$0.74^{+0.74}_{-0.37}$	$0.4^{+0.4}_{-0.2}$



626 GHz

1232 GHz



- **Depletion of Cl/O > 3 wrt protosolar in HCl**

- **Inconsistent with HCl being the main carrier of chlorine in the protosolar nebula**

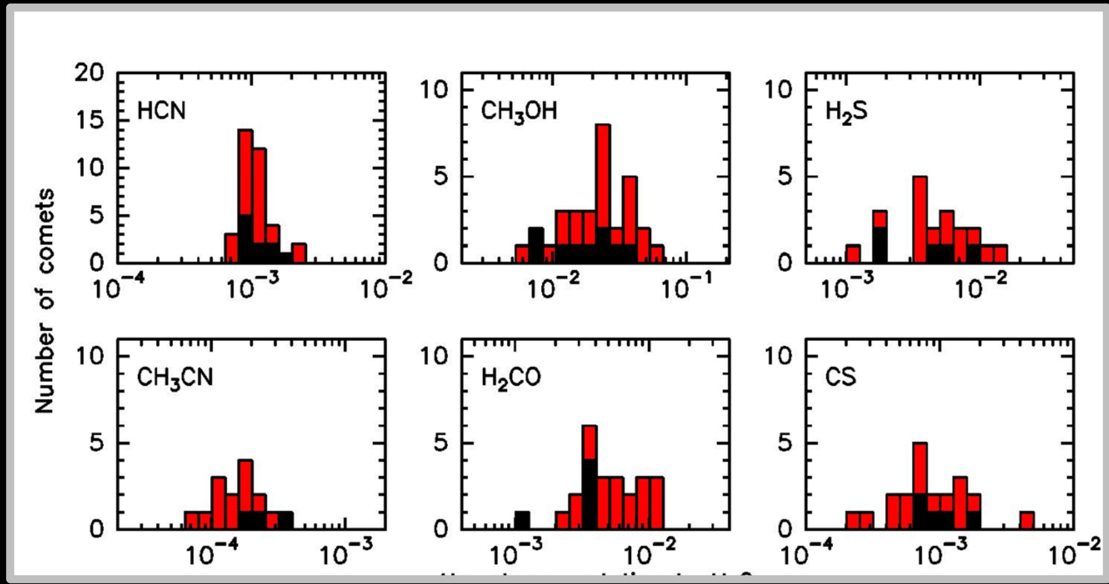
- **Inconsistent with current interpretation of HCl depletion in dense clouds (HCl locked in grains) but in light with HCl in L1157 B1 shock (Codella et al.**

Solar-like HF abundance to be confirmed (Rosetta ?)

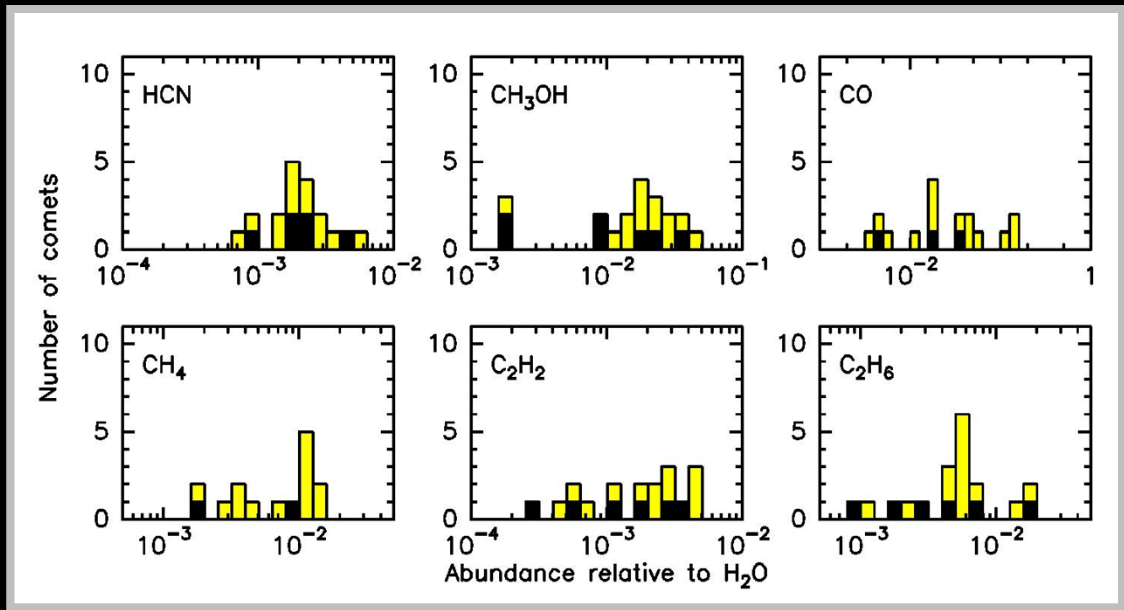
Bockelée-Morvan et al. 2013)

Strong diversity !

Radio data

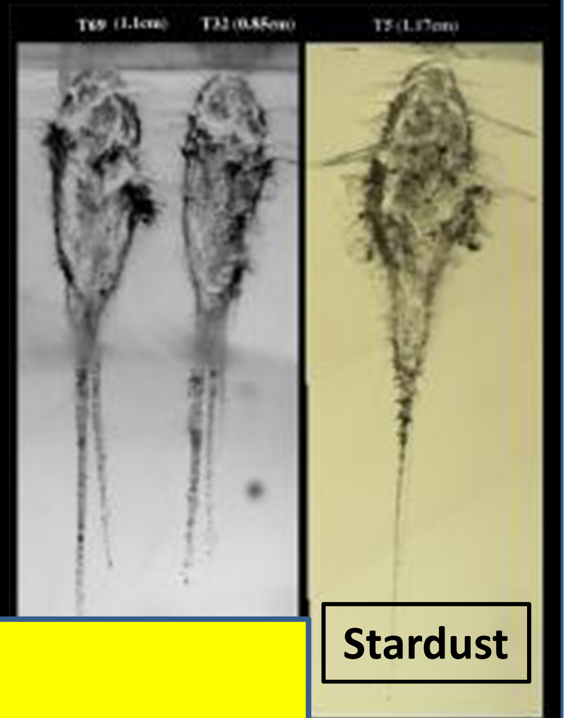


IR data



(in black Jupiter Family comets)

Composition de la matière réfractaire



✓Poussières cométaires: silicates et matière organique

✓Minéraux présents dans les météorites et formés à
haute température

✓Olivine cristalline, anorthite …

✓Inclusions riches en Ca-Al, chondrules

✓ Peu de grains pré-solaires –présence de silicates amorphes d'origine interstellaire

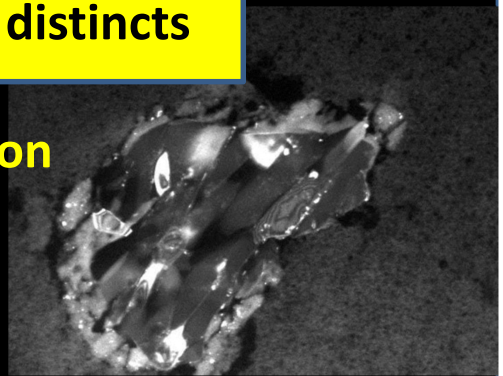
✓ Acides aminés : glycine

• Les comètes ont incorporé des matériaux formés à haute température dans les régions internes de la nébuleuse
• Continuum comètes-astéroïdes - matériaux similaires mais distincts

Important mélange radial dans la nébuleuse avant la formation des comètes

✓Diffusion par turbulence dans le plan du disque

✓Irradiation X des bords du disque

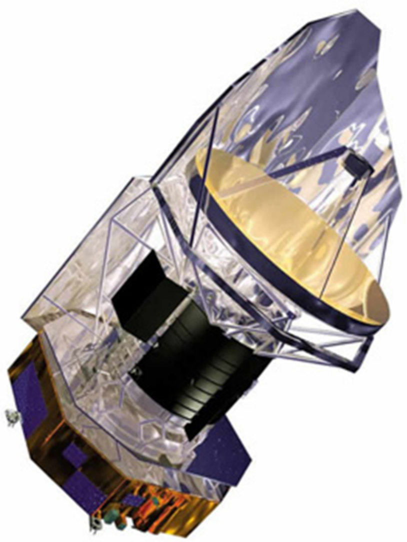


Isotopic ratios : new measurements

Isotopic ratios in comets: key data to constrain the origin of cometary material and Solar System formation

Measurements in cometary atmospheres

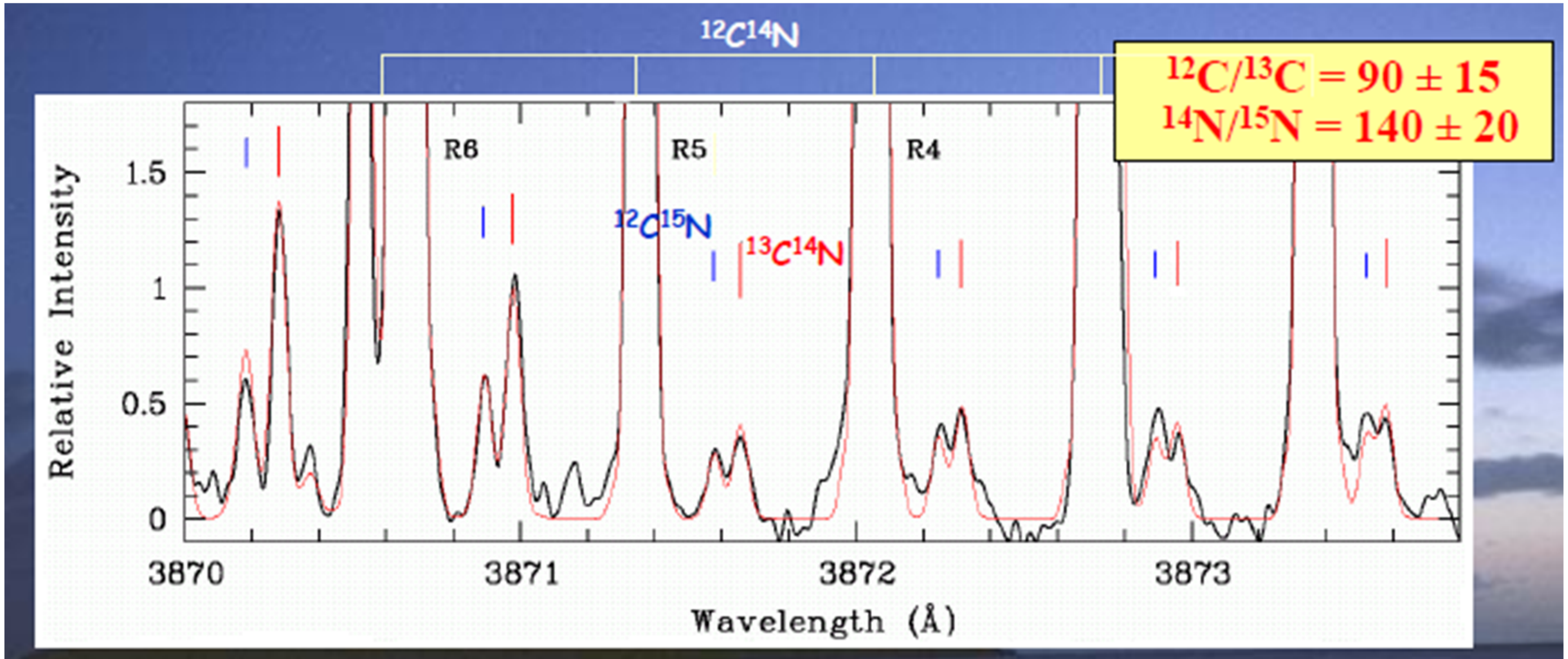
- In situ measurements (mass spectrometers, e.g. Giotto, Rosetta) or sample return
- UV or visible spectroscopy : radicals (CN, C_2, OH, NH_2)
  atoms (D)
- Infrared and radio spectroscopy : molecules, radicals



Measurements are difficult but significant progresses were made recently

UV or Visible spectroscopy

high spectral resolution required



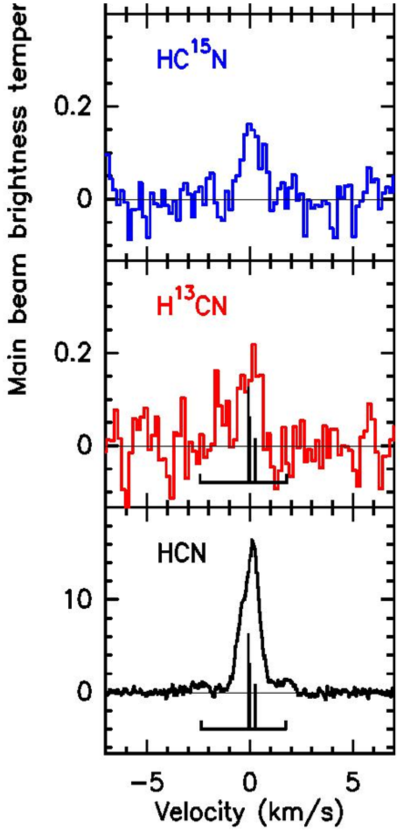
A section of the UVES spectrum of the CN (0,0) violet band in comet 88P/Howell (m_r ~ 8.0).

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

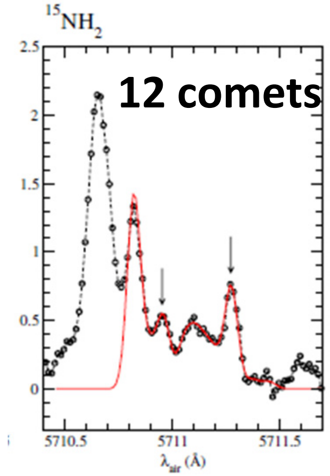
Measurements in HCN

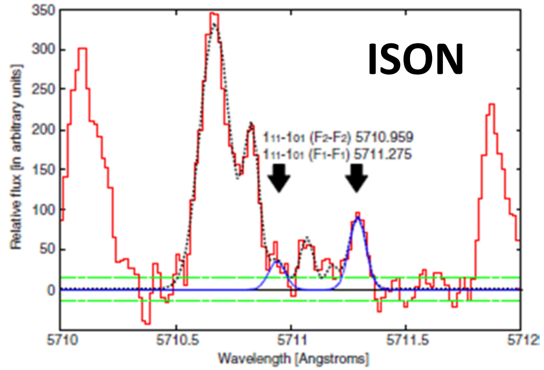


- **17P/Holmes**
  $^{14}N/^{15}N = 139 \pm 26$
- consistent with value in CN

Bockelée-Morvan et al. 2008

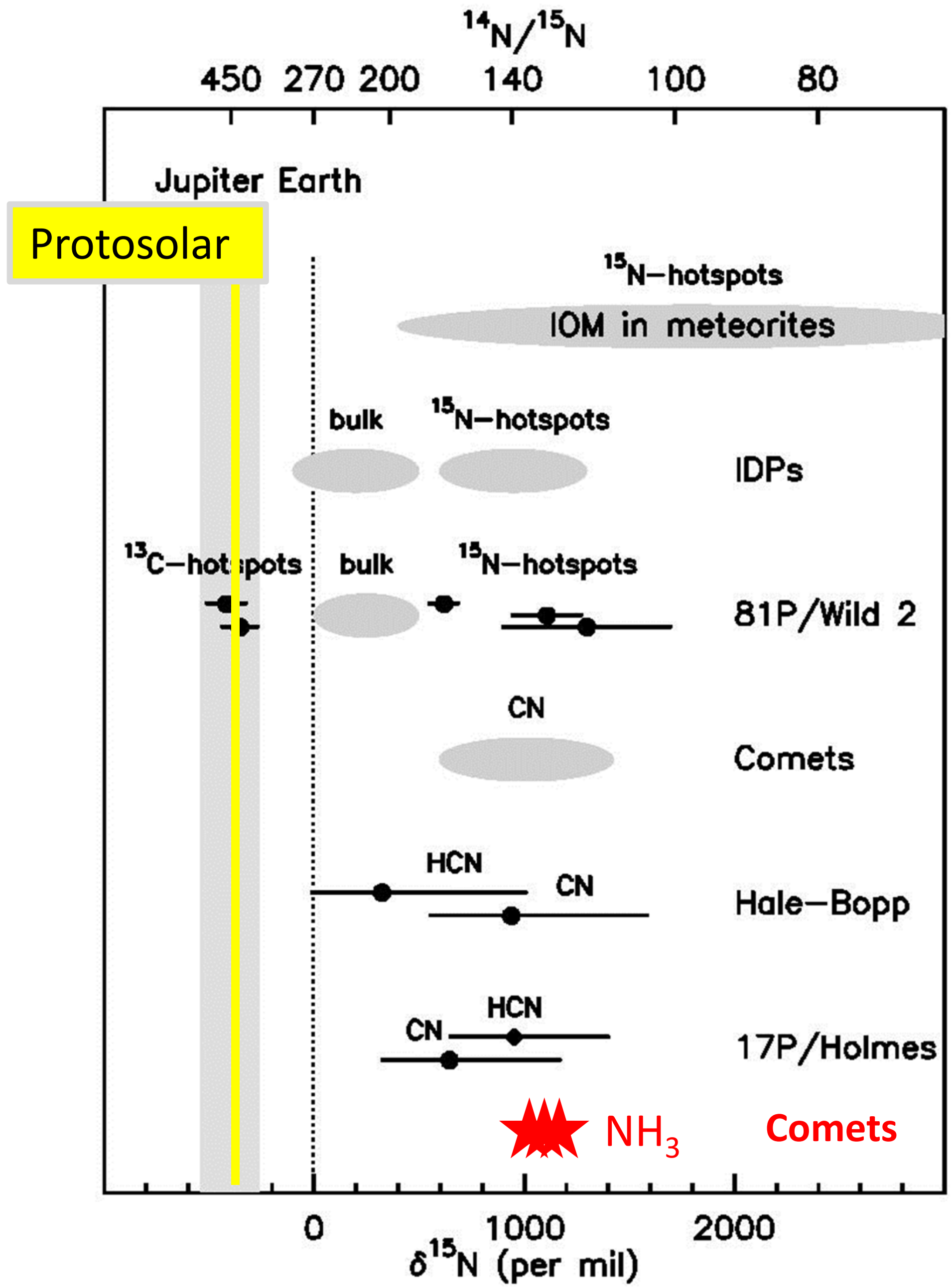
Measurements in NH_3 from NH_2





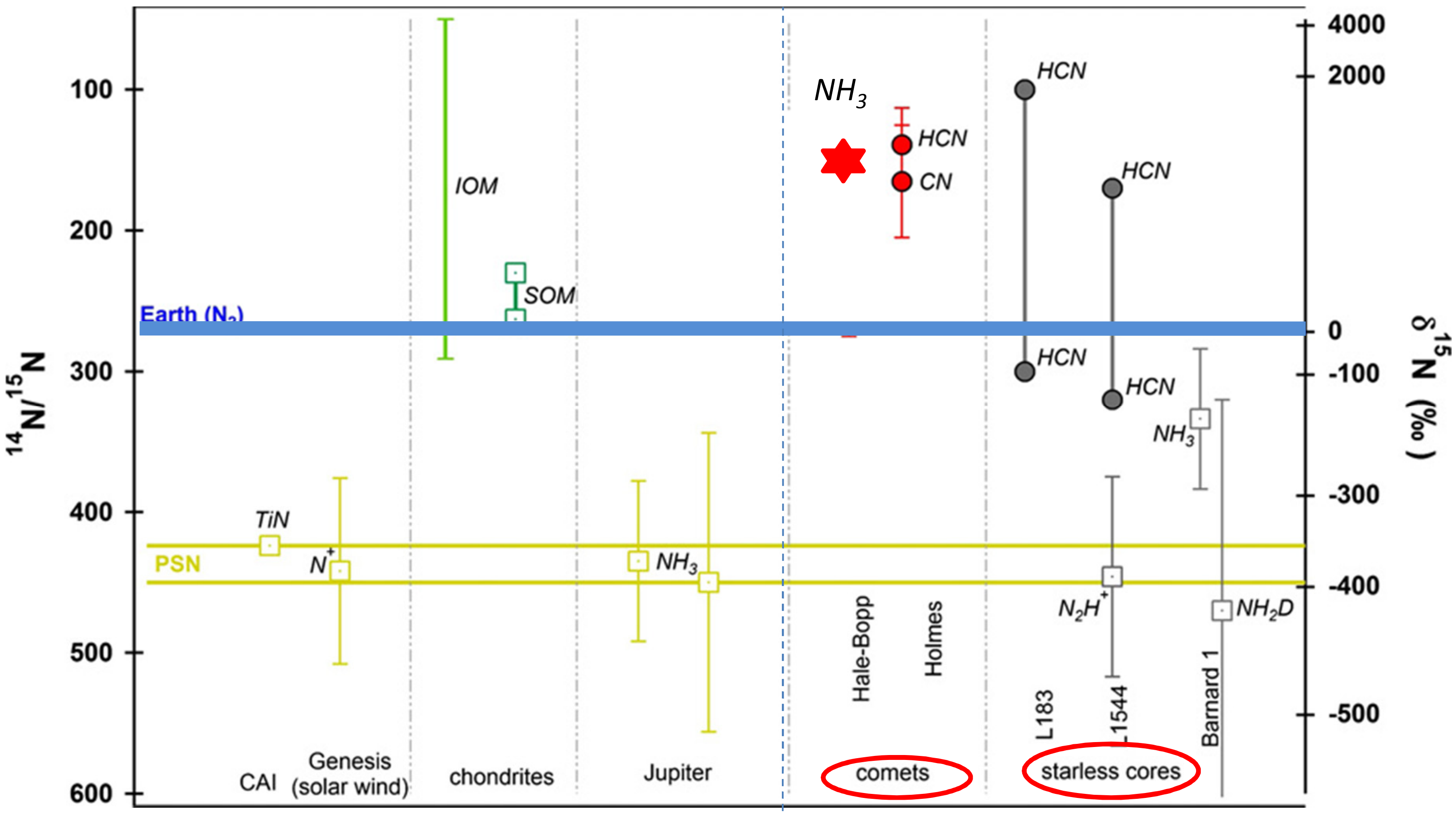
- **12 comets**
  $^{14}N/^{15}N = 130$ (Rousselot et al. 2014)
- **C/2012 S1 (ISON)**
  $^{14}N/^{15}N = 139 \pm 38$ (Shinnaka et al. 2014)
- **C/2012 F6 (Lemmon)**
  $^{14}N/^{15}N = 137 \pm 45$ (Decock et al. This conf)

•Same ^{15}N enrichment in HCN and NH_3
•A factor of two versus Earth value



$^{14}N/^{15}N$
450 270 200 140 100 80
Jupiter Earth
Protosolar
^{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)

Comparison with prestellar cores



Hily-Brandt et al. 2013

Interpretations of ^{15}N enrichment

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

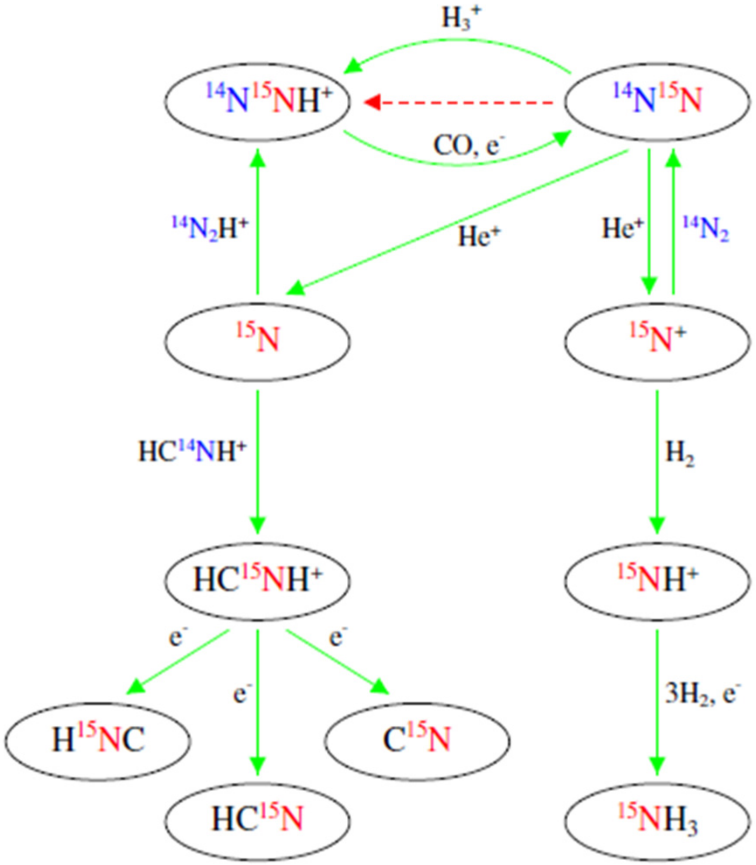
- **Gas-phase chemical models of the ISM** : two pathways for ^{15}N fractionation (Rodgers & Charnley , 2008)
  - to N_2 and NH_3 (slow: 10^6 yr)
  - from N to HCN and other nitriles (rapid: 10^5 yr)

✓ 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)

Interpretations of ^{15}N enrichment

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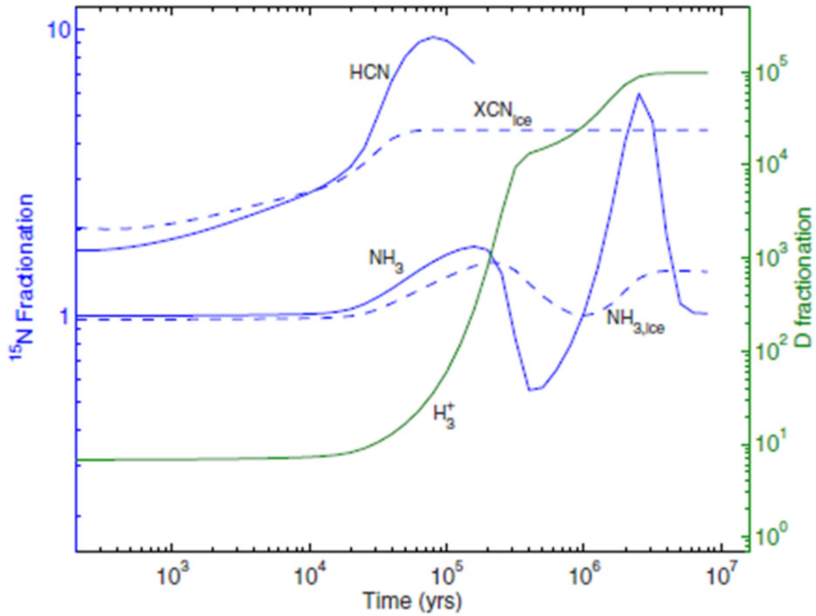
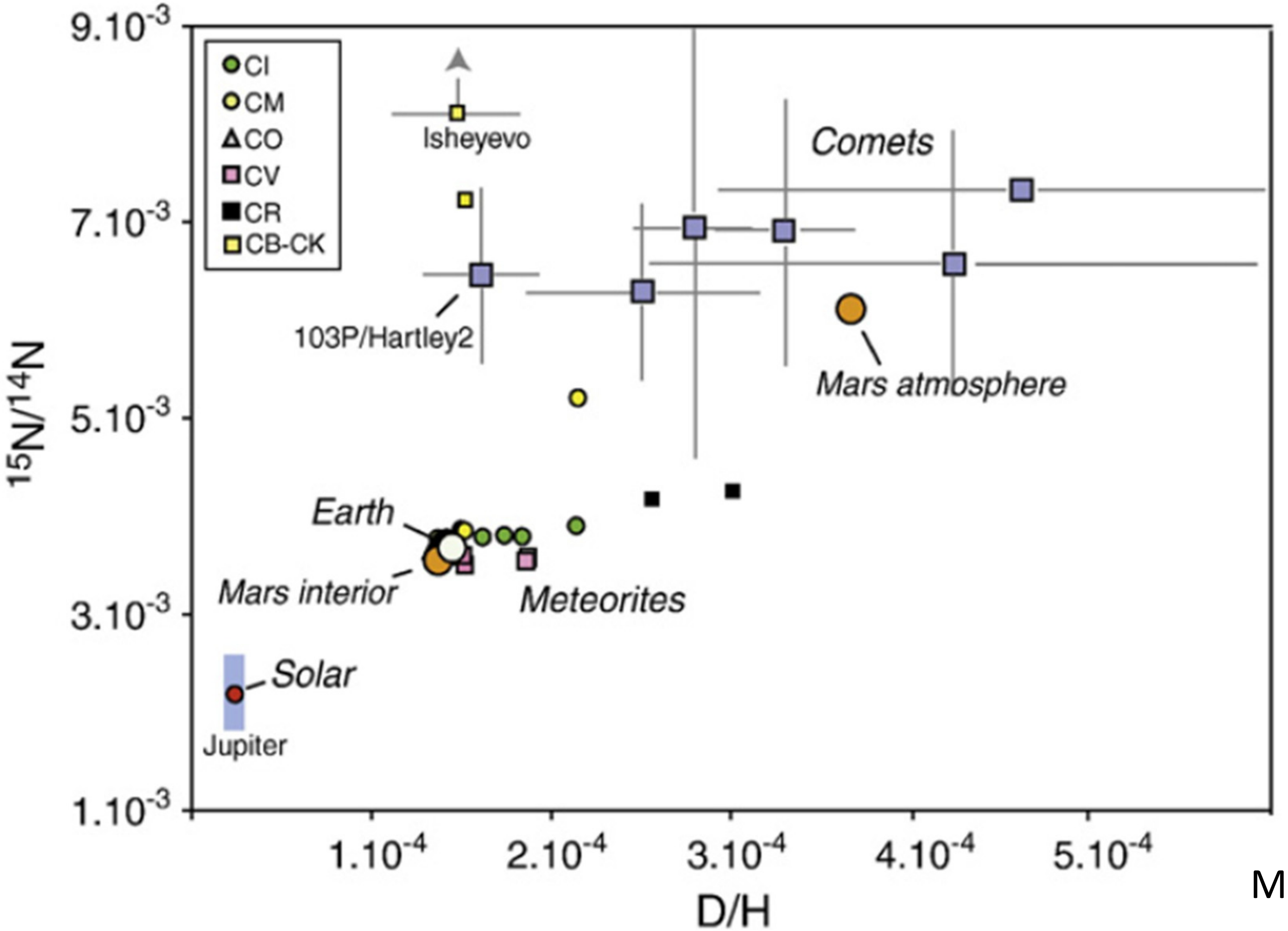
- Models considering self-shielding of N_2 photodissociation (Heays et al. 2014)

✓ explain enrichment in HCN
✓ fractionnation of NH_3 depends on place in the nebula



Wirstrom et al. (2012)

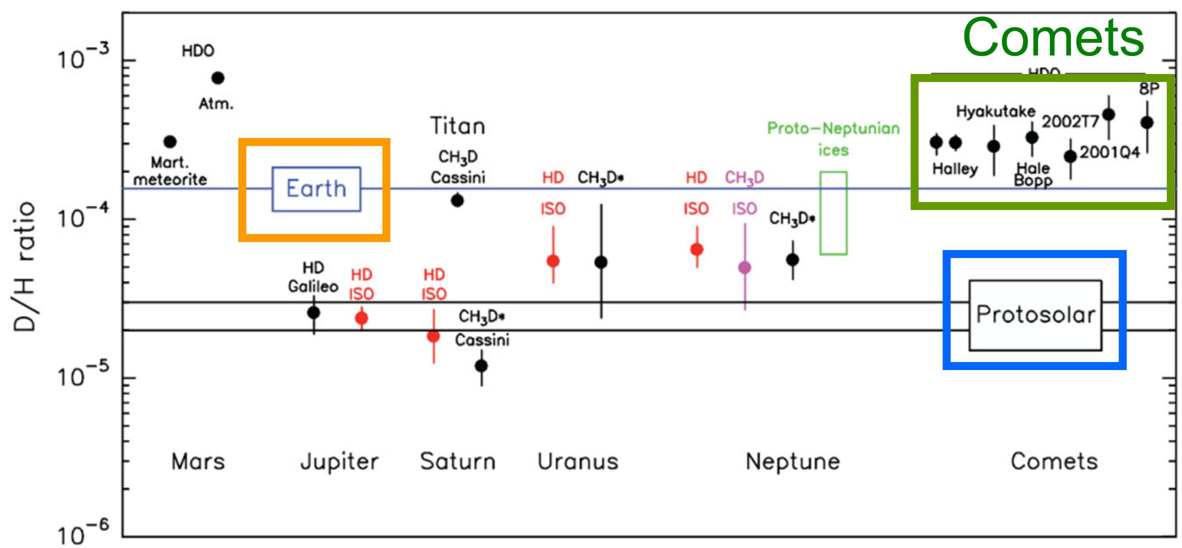
Correlation between D/H & $^{14}N/^{15}N$

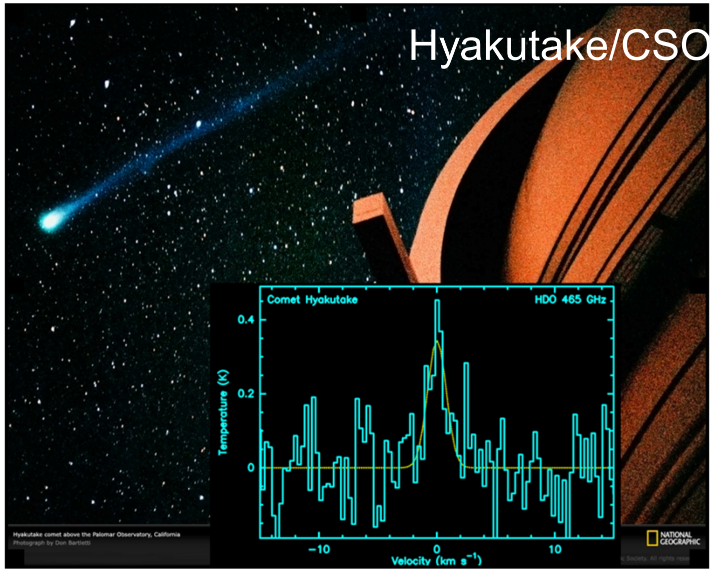


Marty, 2012

Meteorites : ^{15}N and D enrichments do not always correlate : argue against ion-molecule fractionation

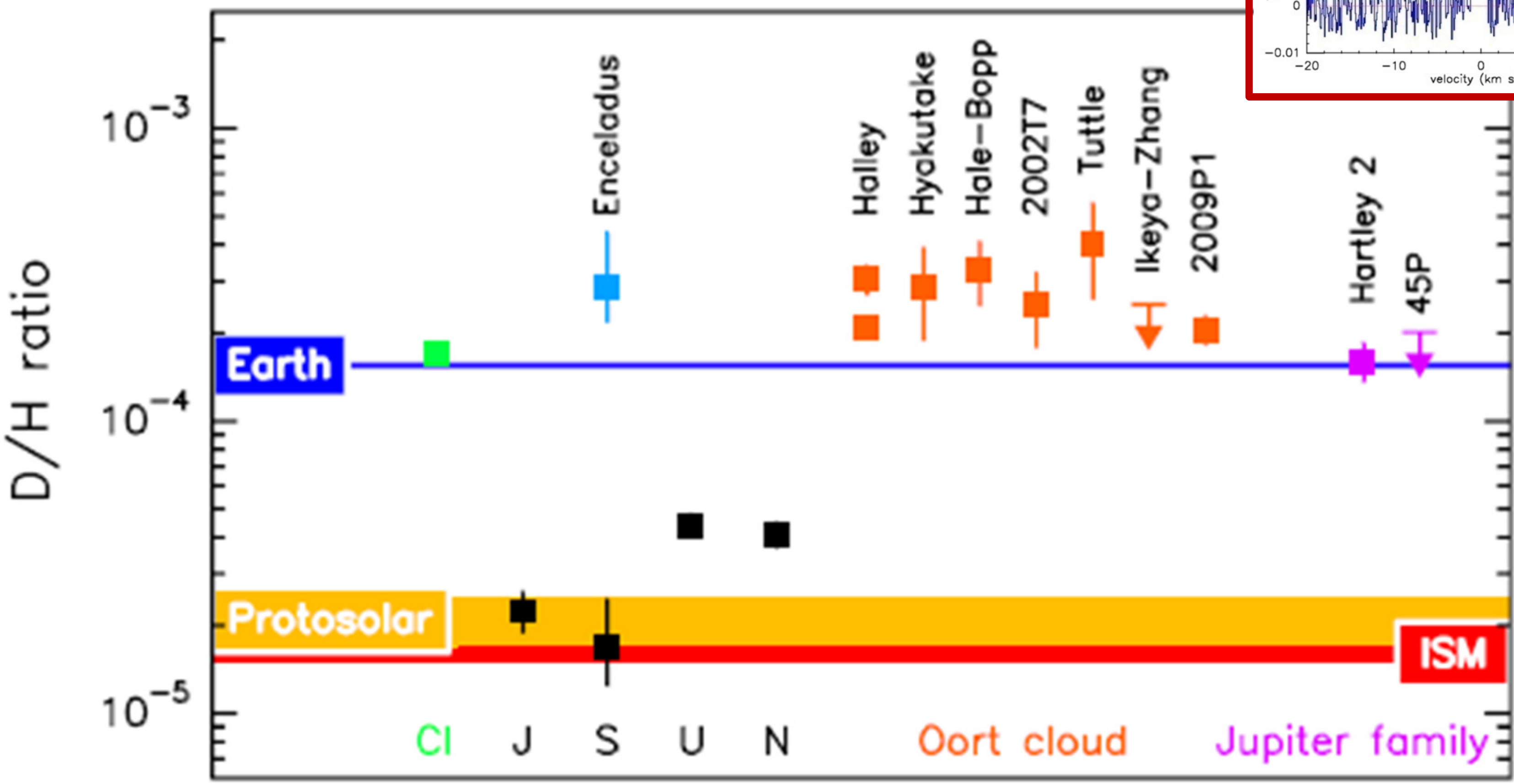
D/H in cometary water (Pre-Herschel)

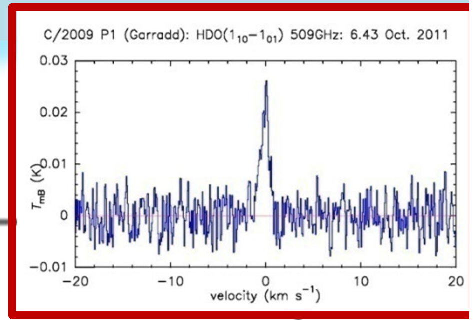




- Protosolar D/H ratio in H_2 is ~$2.5\text{x}10^{-5}$ (same as the Big Bang)
- Earth ocean ratio (Vienna Standard Mean Ocean Water) is $1.56\text{x}10^{-4}$
- D/H measured in several Oort cloud comets is ~$3\text{x}10^{-4}$
- Cometary D/H ratios represent a factor of ~12 enrichment over the protosolar value and 2 times enrichment over the Earth ocean value
- **Based on the isotopic measurements and dynamical models, most probable source of Earth water was ice-rich reservoir in the outer asteroid belt**
- **Comets could have contributed less than 10% of the Earth water**

Deuterium in water – the post-Herschel view

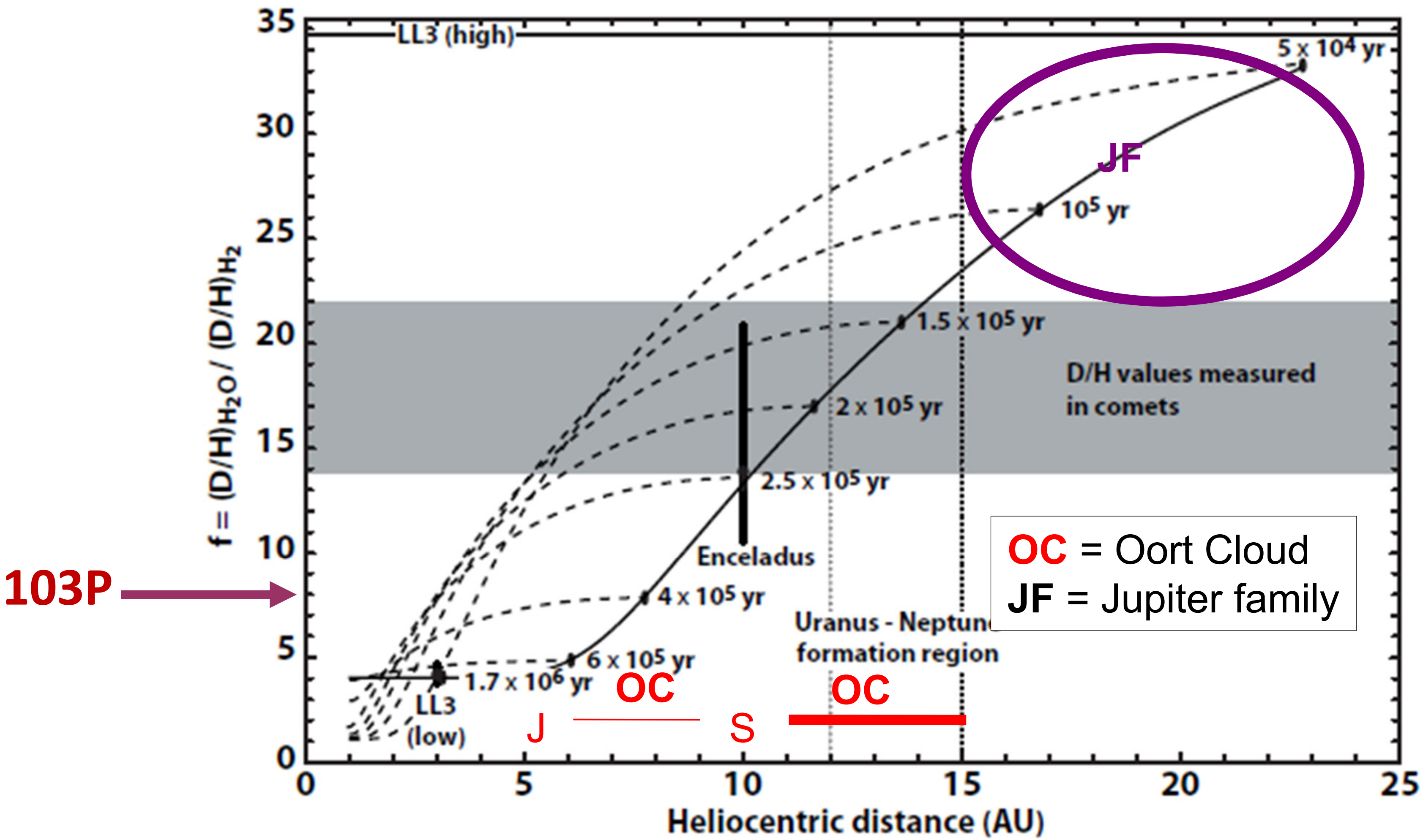




Lis et al. (2013)

Model Predictions for D/H in comets

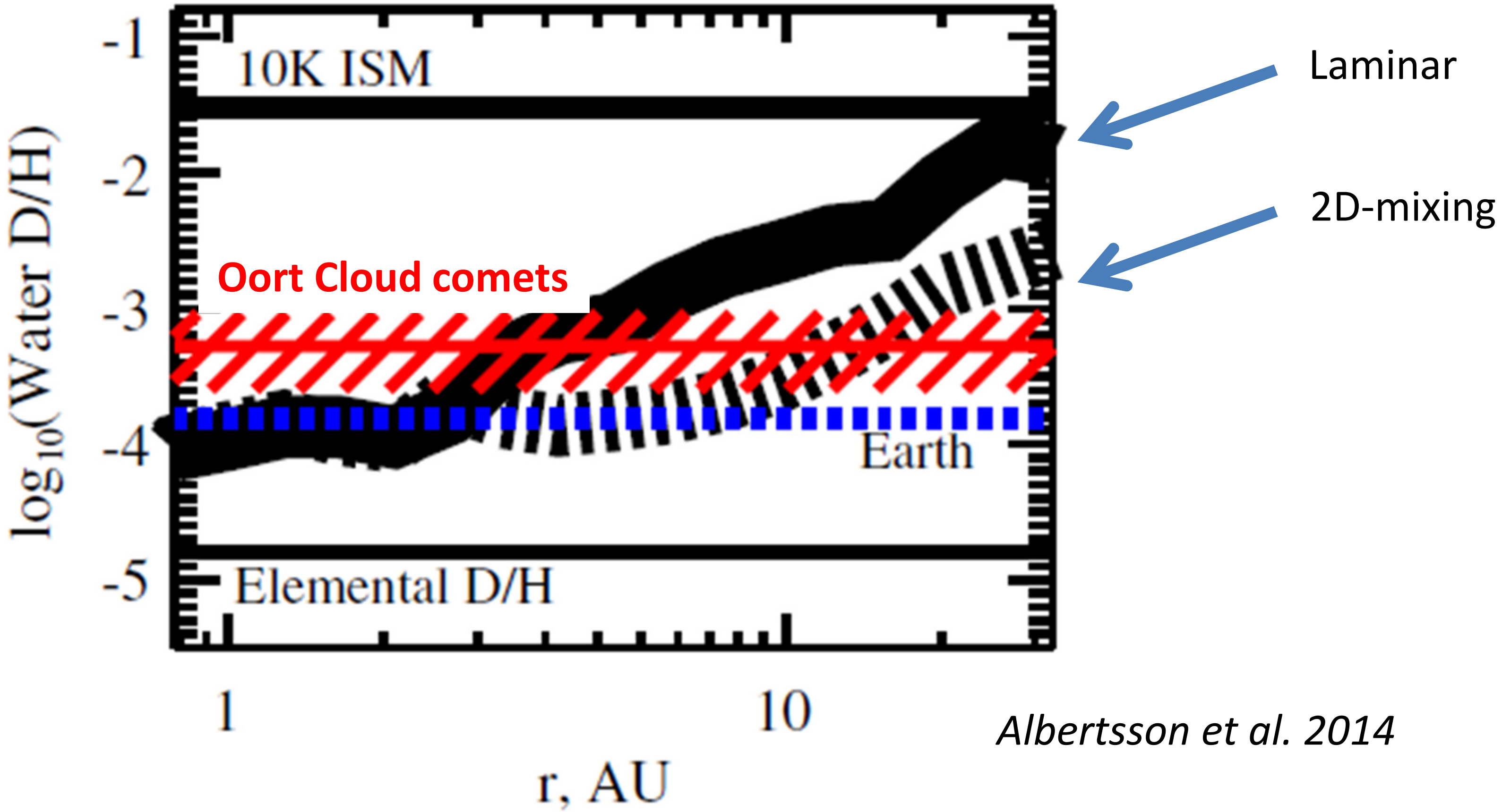
- isotopic exchange between H_2O and HD and turbulent mixing in an evolving Solar Nebula
- the Solar Nebula is here not anymore accreting mass from the presolar cloud



Takes into account planet migration

Kaveelars et al. (2011)

Model Predictions for D/H in comets

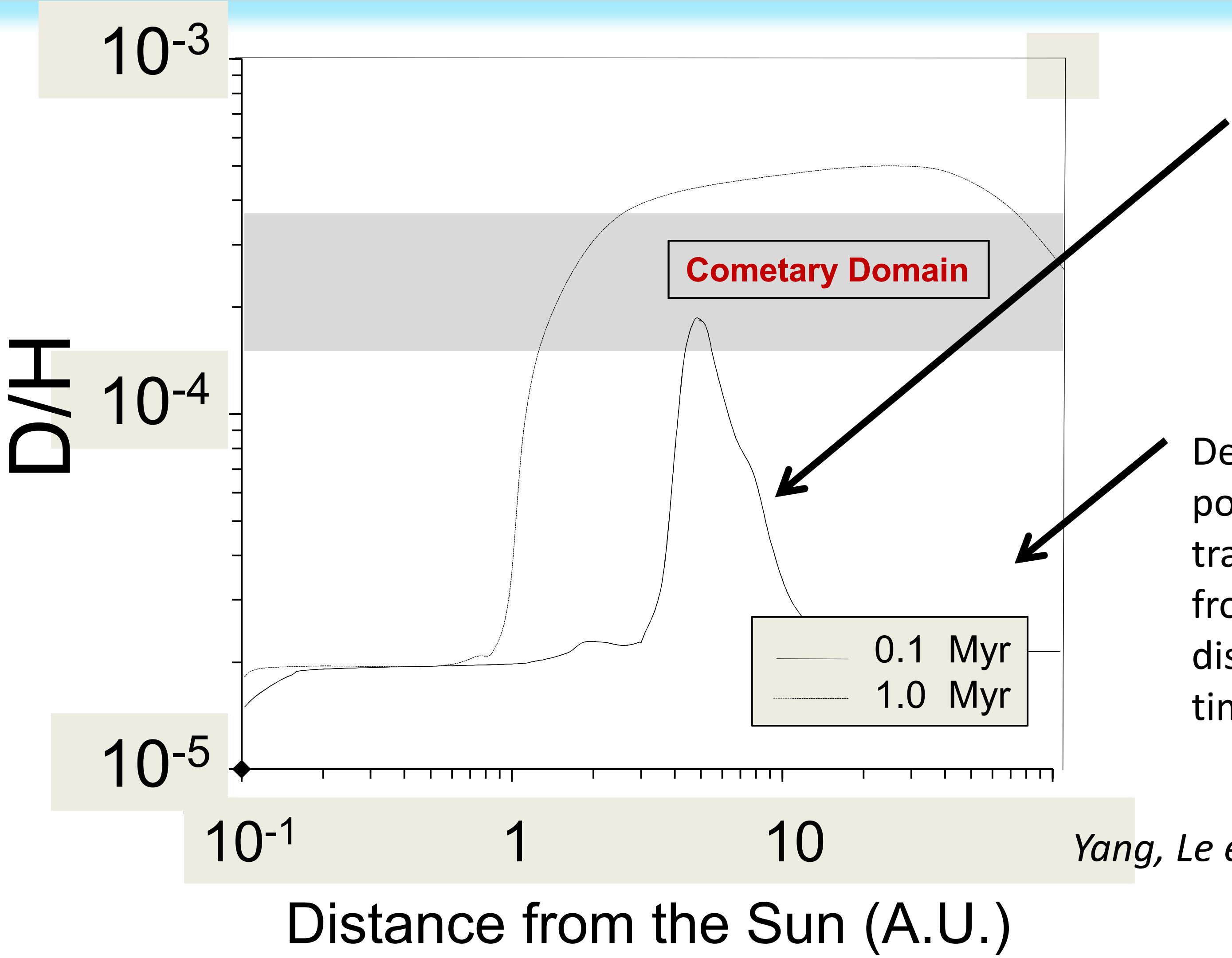


Albertsson et al. 2014

- **Steady state solar nebula model**
- **Time-dependent gas-grain chemical model with turbulent mixing**

-> Mixing model favored over laminar model

Model Predictions for D/H in comets



Deuterium rich water feeding the disk

Deuterium poor water transported from the inner disk at early times

Yang, Le et al. 2013

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

What are the implications ?

- **Current understanding of deuteration in different solar system reservoirs, or *solar system dynamics*, is incomplete and has to be revisited**

  - ***Ices condensed close to the Sun would be more deuterated?***

  e.g., out of equilibirium chemistry at high T $H_2/H_2O/OH/H/O$ (Thi et al. 2010)

  – but seems incompatible with D/H in carbonaceous chondrites

  - ***D/H in outer disk lower than in the inner regions : recent model of Yang et al.***
  - ***Revisit origin of JFCs and Oort Cloud comets ?***

  JFC = Troyans formed in the vicinity of Jupiter (Horner et al. 2007) ?

  90% of Oort cloud comets from other stars in the Sun's birth cluster (Levison et al. 2010)?

- **There is diversity in the D/H ratio in the comet population**

  Is the dichotomy between JFC and OCC real ?

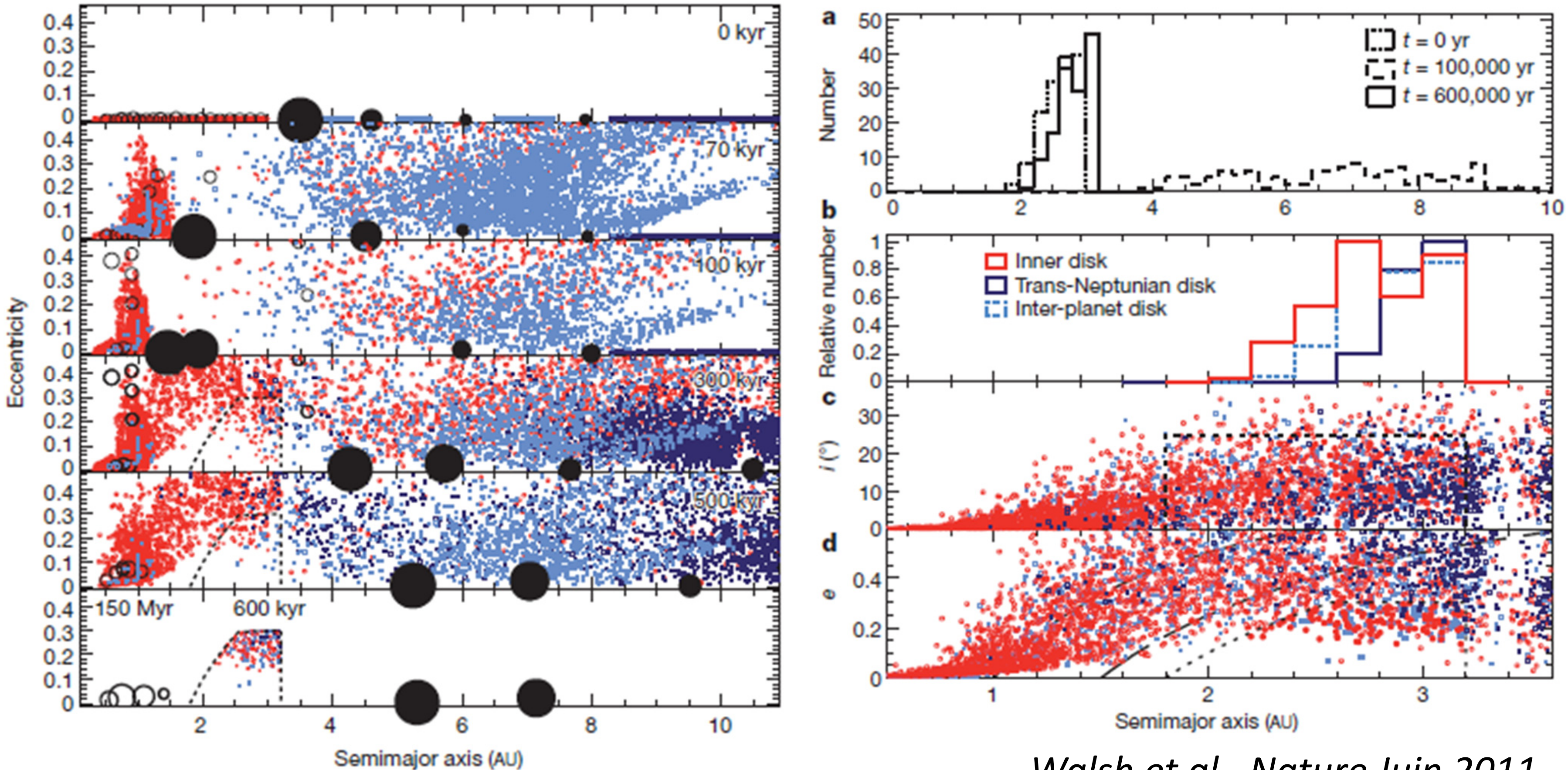
  Diversity within the two populations expected from Grand Tack model (Walsh et al. 2011)

- **There is a continuum between asteroids and comets:**

  the low D/H in JFCs would argue for formation closer to the Sun …

- **The reservoir of icy bodies with Ocean-like water is larger than previously thought and comprises likely the Kuiper belt**

Radial mixing of planesimals - Grand Tack model

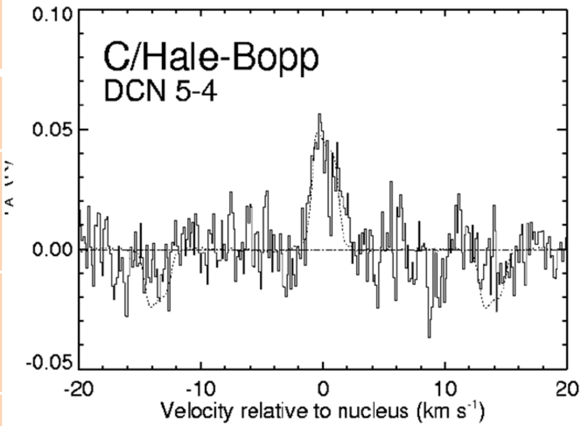


Walsh et al., Nature Juin 2011

- **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

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

Conclusions

- **Several key measurements in the recent years**

- **Isotopic diversity in the Solar System is far to be understood**

- **New measurements expected**

- ALMA , near-IR, UV investigations

- Rosetta

✓D/H (H_2O and other species)
✓$^{14}N/^{15}N$ (in HCN, CN, NH_2 …)
✓Probe the diversity in comet population