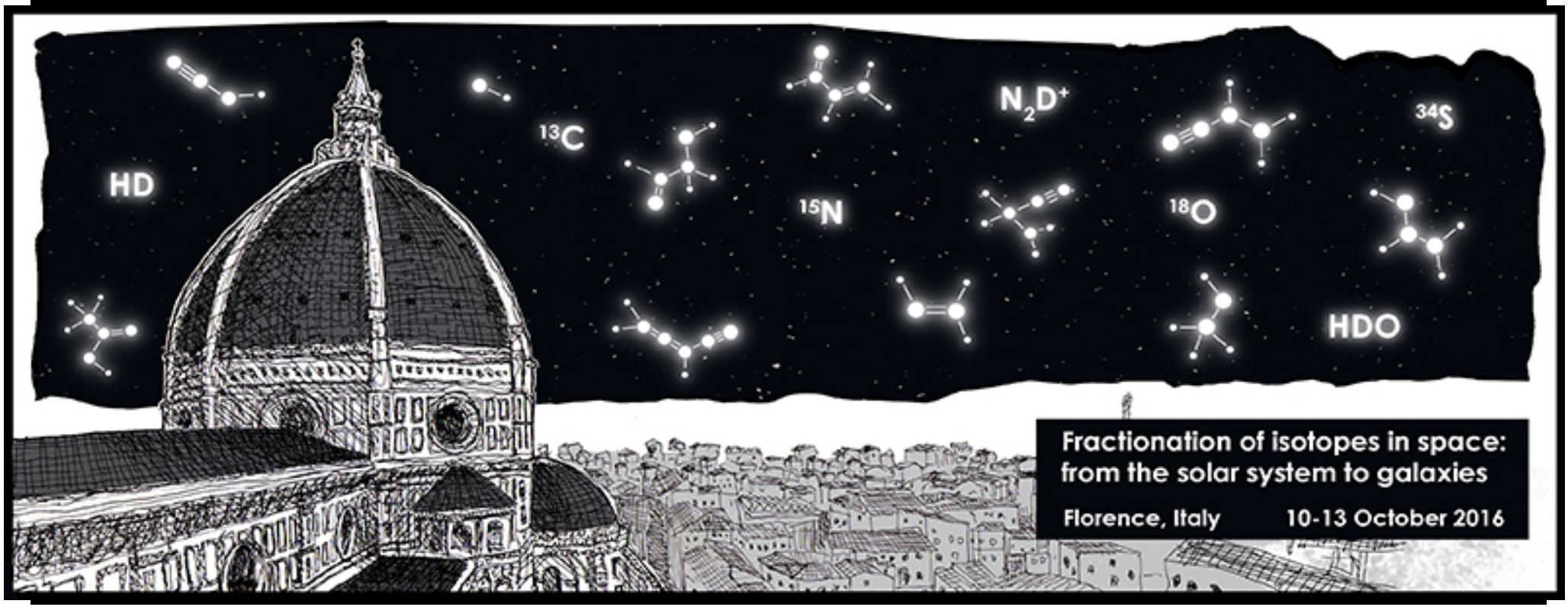
Fractionation of Deuterium (and other elements)

Francesco Fontani – INAF-Arcetri



Overview

1) Isotope fractionation

2) Deuterium fractionation

3) Deuterium fractionation in star-forming regions

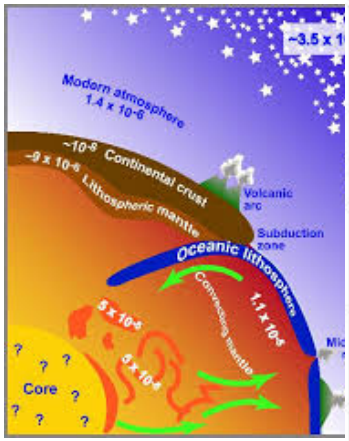
4) Fractionation of Nitrogen

5) Summary, conclusions, recommended reading

Isotopic fraction

Def: **abundance ratio** between two **stable isotopes** of an element

On Earth



Element	δ value	Ratio Measured (R)	International Standards	R, International Standards
Hydrogen	δD	$^{2}H/^{1}H$	Vienna Standard Mean Ocean Water (VSMOW)	0.00015575
		$^{2}H/^{1}H$	Standard Light Antarctic Precipitation (SLAP)	0.000089089
Carbon	$\delta\,^{13}C$	$^{13}C/^{12}C$	Vienna Pee Dee Belemnite (VPDB)	0.0112372
Nitrogen	$\delta\,^{15}N$	$^{15}N/^{14}N$	Air	0.003676
Oxygen	$\delta\,^{18}O$	$^{18}O/^{16}O$	Vienna Standard Mean Ocean Water (VSMOW)	0.0020052
		$^{18}O/^{16}O$	Vienna Pee Dee Belemnite (VPDB)	0.0020672
		$^{18}O/^{16}O$	Standard Light Antarctic Precipitation (SLAP)	0.0018939
Sulfur	$\delta\,^{34}S$	$^{34}S/^{32}S$	Canyon Diablo Triolite (CDT)	0.045005

Colorado Plateau Stable Isotope Laboratory

Isotopic fraction

Def: **abundance ratio** between two **stable isotopes** of an element

In the local ISM

Different from Terrestrial Standards by a factor 10!

D/H ~ 1.5 10-5 (Oliveira+03, Linsky+06)

Isotope	Galactic center	4 kpc molecular ring	Local ISM[b]	Solar System[c]	Carbon stars[d]	Nuclei of galaxies
$(^{12}C/^{13}C)$	~ 20	53 ± 4^{b}	77 ± 7^{b}	89	> 30	~ 40[h]
$(^{14}N/^{15}N)$	> 600	375 ± 38^{b}	450 ± 22^{b}	270	> 515	...
$(^{16}O/^{18}O)$	250	327 ± 32^{b}	560 ± 25^{b}	490	320 to 1260 > 2700	~ 200[i]
$(^{18}O/^{17}O)$	3.2 ± 0.2^{e}	3.2 ± 0.2^{e}	3.2 ± 0.2^{e}	5.5	0.6 to 0.9 < 1	8[i]
$(^{32}S/^{34}S)$	~ 22[f]	~ 22[f]	~ 22[f]	22	...	...
$(^{29}Si/^{30}Si)$	1.5[g]	1.5[g]	1.5[g]	1.5	...	...

Wilson & Rood 1994, ARA&A

Similar to Terrestrial Standards (within a factor ~3)

Isotopic fractionATION

Def: the chemical process by which **isotopic fractions in molecules (can) vary** through chemical reactions

e.g. (1) $^{12}CO + {}^{13}C^{+} \longleftrightarrow {}^{12}C^{+} + {}^{13}CO$ + 35 K

The **difference in molecular binding energy** between reactants and products , caused by different zero-point vibration energy, **makes one direction exothermic, i.e. favoured in cold gas:**

Zero-point energy of a biatomic molecule

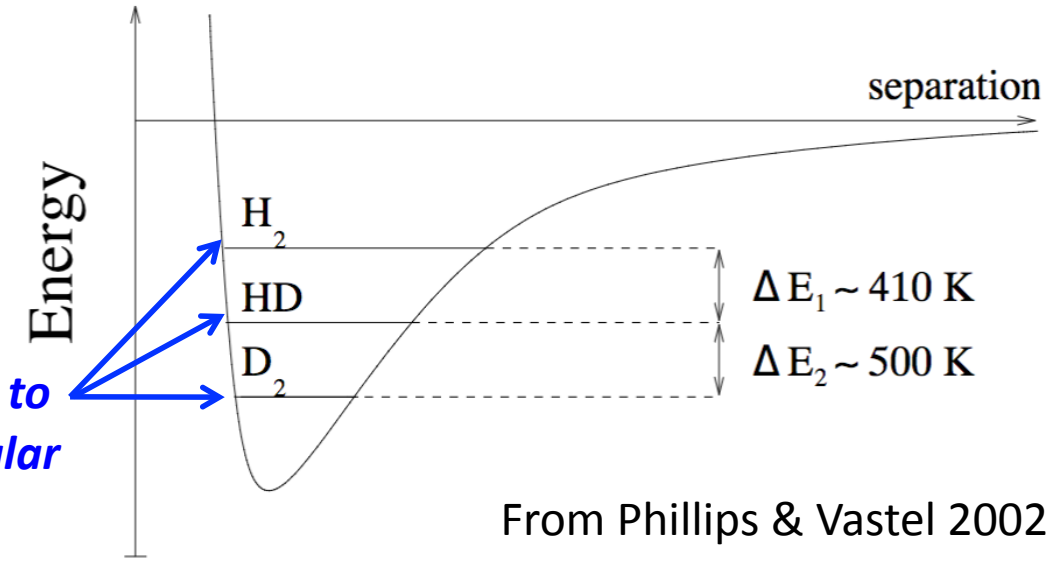
$$E_v \approx \frac{1}{2} h \left(1/2\pi \sqrt{\frac{k}{m_r}} \right)$$

→ **The molecule with heavier isotope has lower zero-point energy**

Deuterium fractionation

- Deuterium is formed during the Big Bang, and destroyed into stars
- In molecular clouds, atomic D initially goes into HD (and D_2) through:

$$D^+ + H_2 \longrightarrow HD + H^+ + \Delta E_1$$
$$D^+ + HD \longrightarrow D_2 + H^+ + \Delta E_2$$



Zero-point energies relative to The minimum of the molecular Potential curve

From Phillips & Vastel 2002

- since D-molecules have lower zero-point energy, **in cold environments (T < 50 K) fractionation favours formation of HD and D_2**, because:

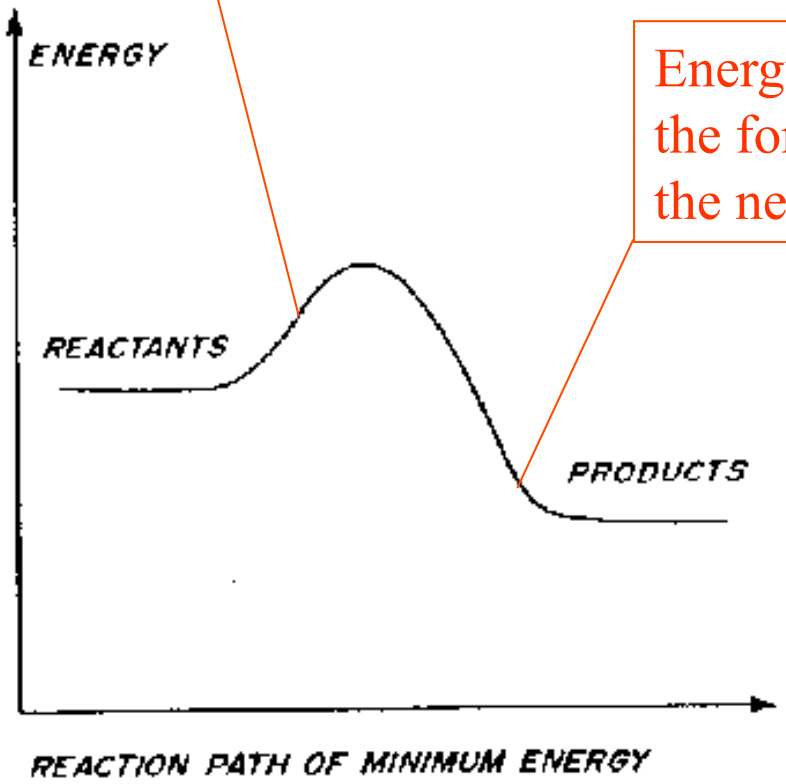
$$k_{<--} = k_{-->} \exp\left(\frac{-\Delta E}{T}\right)$$

Why are ion-neutral reactions important?

Neutral-neutral: A + BC → AB + C

Minimum energy to brake bonds

E ~ 0.1-1 eV



Energy released by the formation of the new bond

$k_b T$ ~ 0.01 eV @ 100 K: in cold molecular clouds the barrier cannot be overtaken…

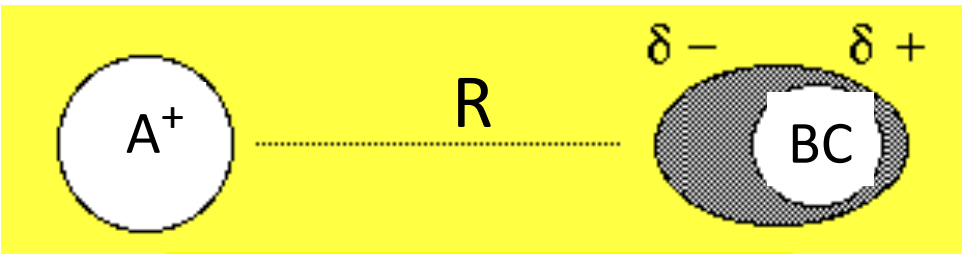
Neutral-neutral important in warm (T > 100 K) gas only

e.g. Duley & Williams 1984, "Interstellar chemistry"
Van der Tak 2005

Why are ion-neutral reactions important?

Ion-neutral: $A^+ + BC \rightarrow AB^+ + C$

Exothermic ion-molecule reactions can occur even in very cold (T < 90 K) gas because **the ACTIVATION BARRIER is OVERTAKEN** by the energy of the long-range attractive interaction between the ion and the dipole moment induced in the neutral particle.



$$V(R) = -\alpha e^2/2R^4$$

Ion-neutral dominant in cool (T < 100 K) gas

e.g. Herbst & Klemperer 1973; Anicich & Huntress 1986

Deuterium fractionation

Roberts & Millar 89; Gerlich+02; Asvany+04; Gerlich & Schlemmer 02; Flower+06

1. If $T \leq 30$ K

$$H_3^+ + HD \longrightarrow H_2D^+ + H_2 + 230K$$

$$CH_3^+ + HD \longleftrightarrow CH_2D^+ + H_2 + 390K$$

$$C_2H_2^+ + HD \longleftrightarrow C_2HD^+ + H_2 + 550K$$

H_2D^+/H_3^+ increases in cold gas
(>> D/H cosmic abundance ~10^{-5})

Deuterium fractionation

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2. If CO freezes-out (i.e. $n \geq 10^5$ cm^{-3})

$$\cancel{H_2D^+ + CO \longleftrightarrow DCO^+ + H_2}$$

H_2D^+ combines with other neutrals, X,
Increasing $[XD^+]/[XH^+]$ ratios
(e.g., $X = N_2 \rightarrow N_2D^+/N_2H^+ \sim 0.1$)

Deuterium fractionation

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3. If o-/p-H_2 is low H_2D^+/H_3^+ is high

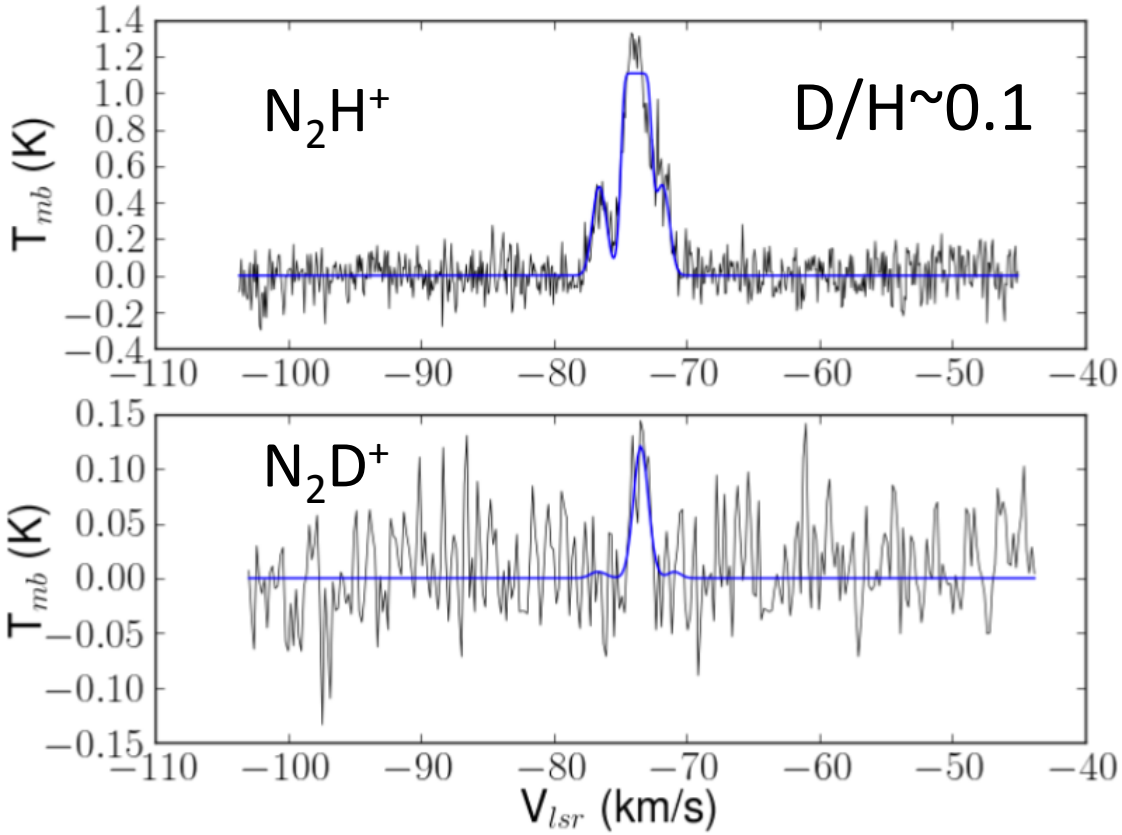
$$H_3^+ + HD \longleftarrow H_2D^+ + o\text{-}H_2$$

Internal energy of o-H_2 170K higher than p-H_2

Observations of D-molecules

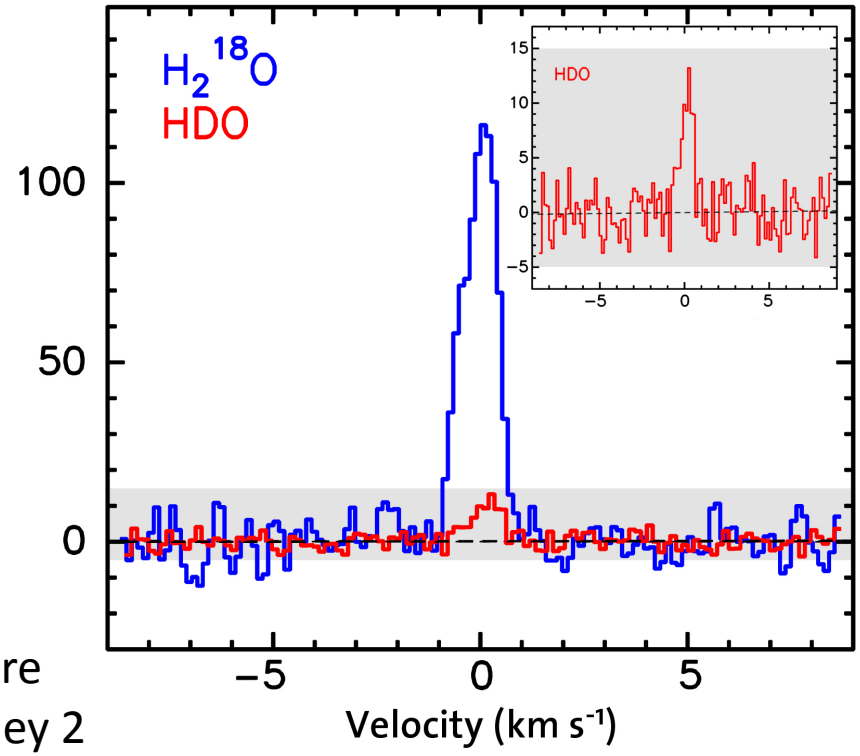
Parise+02;+04;+06; Caselli+03;+08; Ceccarelli+12; Coutens+13 Tan+13; Codella+16

Singly-deuterated



Lackington+16, MNRAS
IRDC SDC329.313

D/H~1.5 10^{-4}
....terrestrial!!

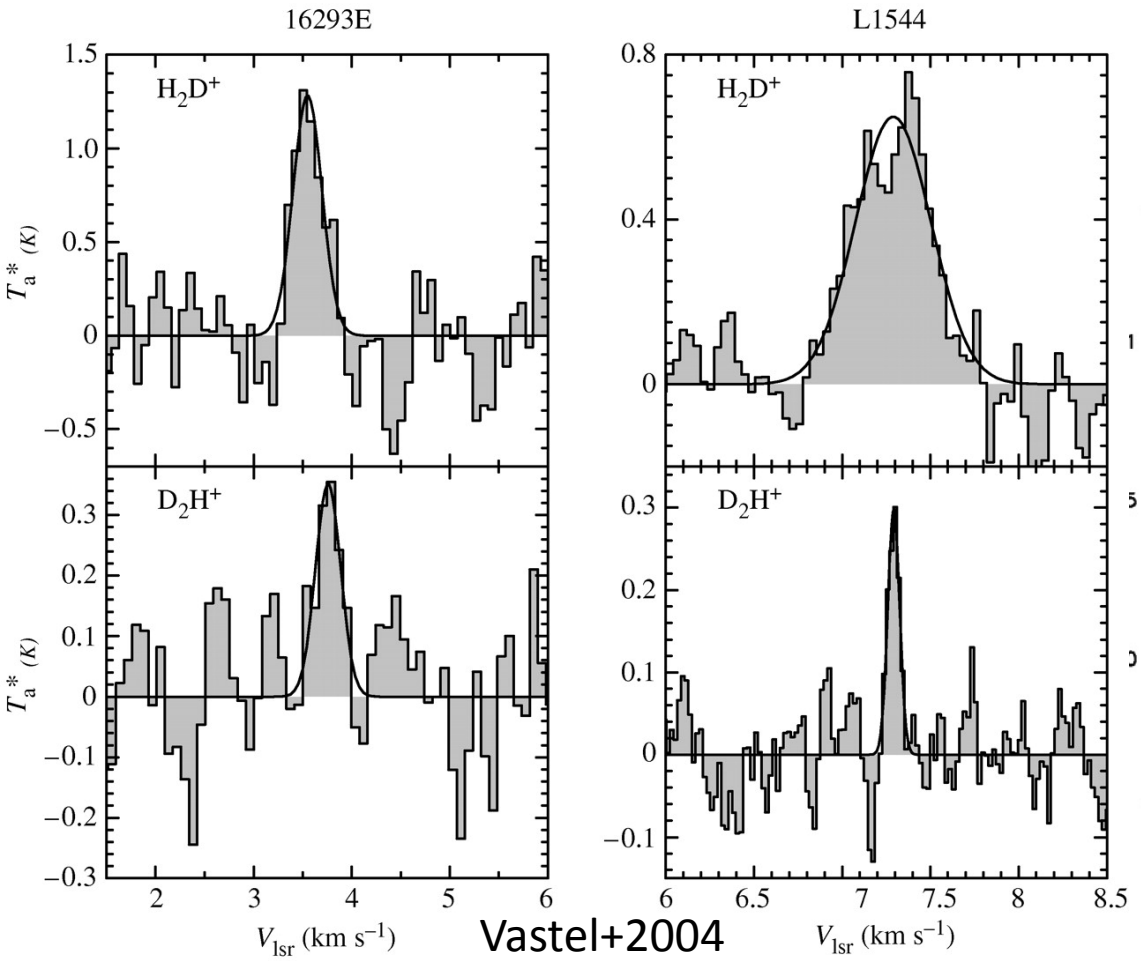


Hartogh+11, Nature
Comet 103P/Hartley 2

Observations of D-molecules

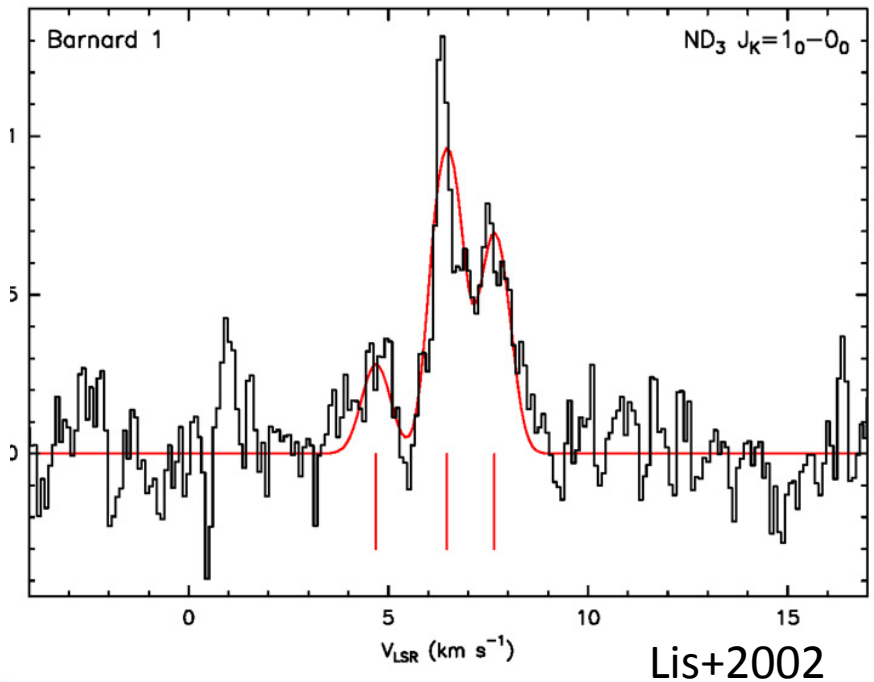
Ceccarelli+98;+12; Parise+02;+04;+06; Caselli+03;+08; Tan+13; Codella+16

Doubly-deuterated



Vastel+2004

Triply-deuterated

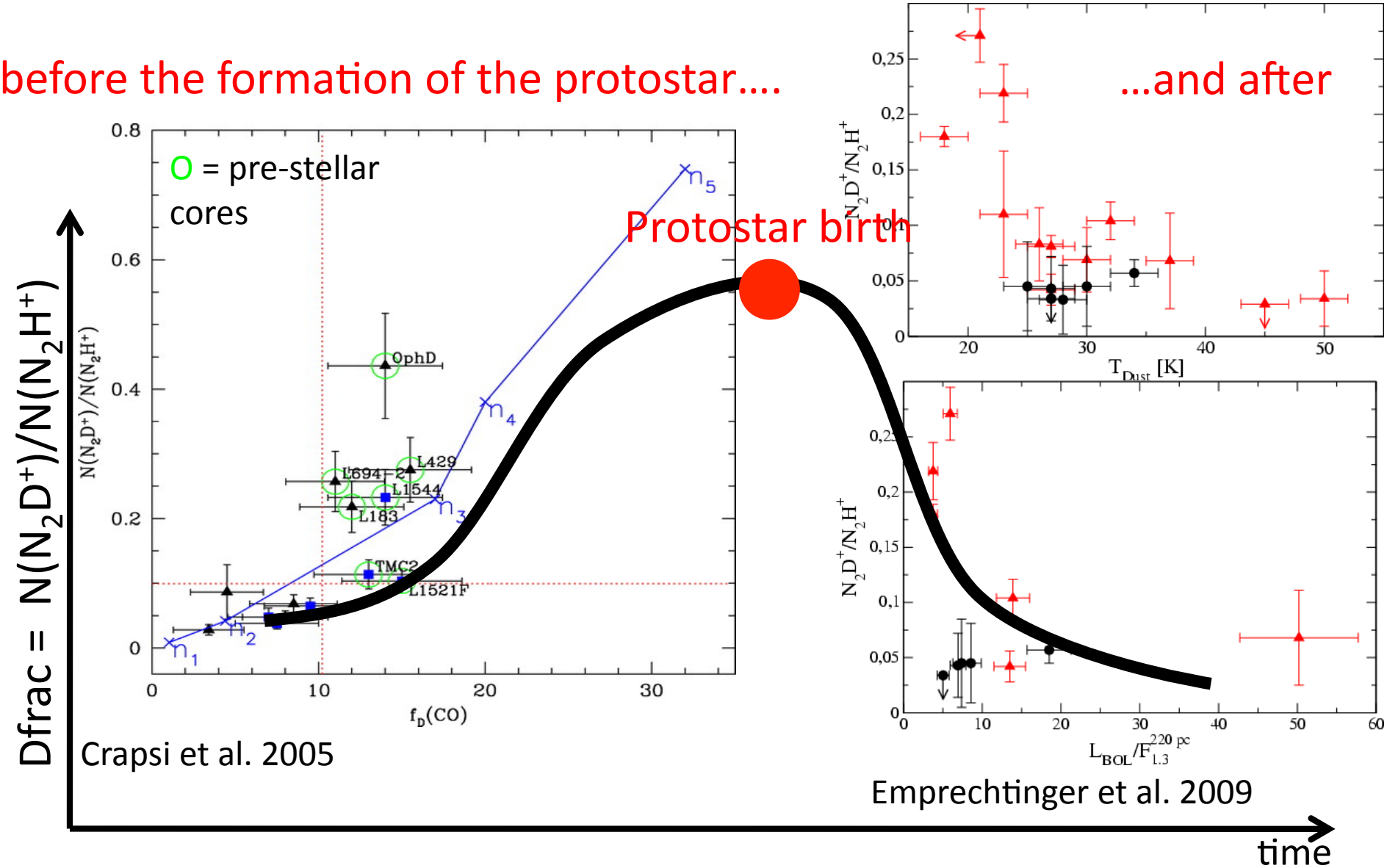


Lis+2002

$N(N_2D^+)/N(N_2H^+)$ in low-mass SF cores

before the formation of the protostar....

...and after

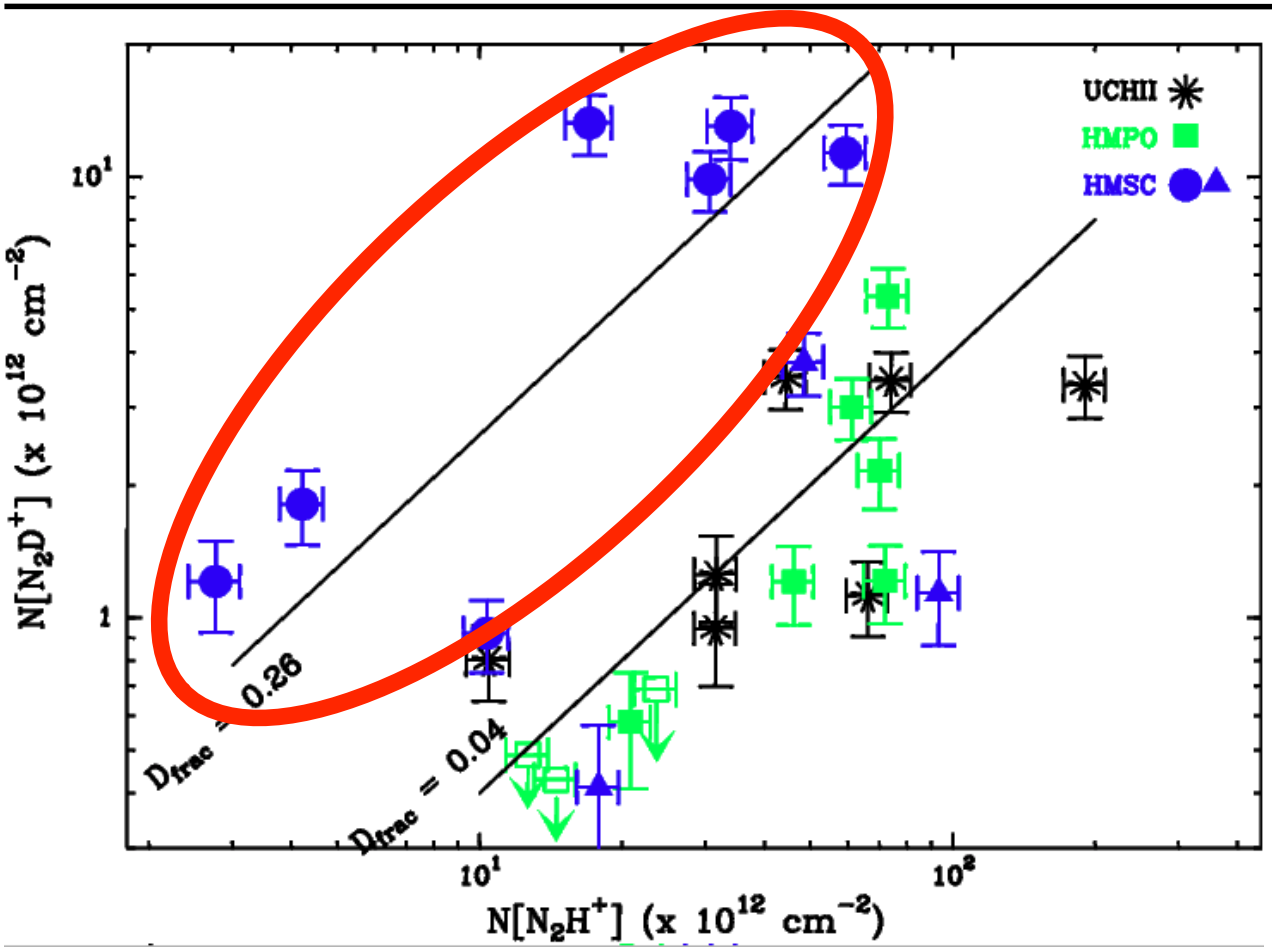


Crapsi et al. 2005

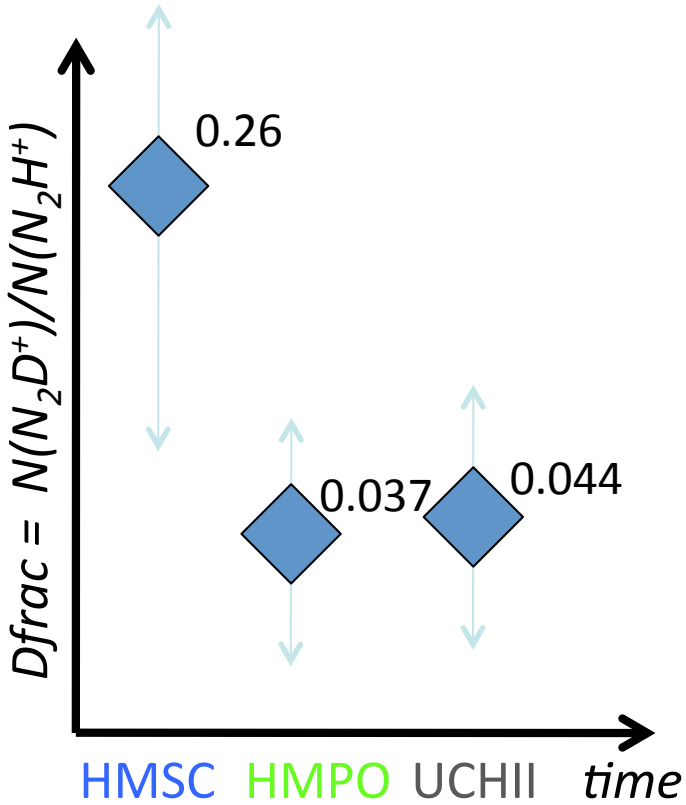
Emprechtinger et al. 2009

$N(N_2D^+)/N(N_2H^+)$ is an evolutionary tracer in low-mass SF cores!

$N(N_2D^+)/N(N_2H^+)$ in high-mass SF cores



Fontani et al. 2011, A&A, 529, L7



Statistical separation between HMSCs and HMPOs/UCHIIs:
Kolmogorov-Smirnov test: P ~ 0.004

$N(N_2D^+)/N(N_2H^+)$ is an evolutionary tracer in high-mass SF cores!

Formation of D-molecules

GAS

Roberts & Millar 89; Gerlich+02; Asvany+04; Gerlich & Schlemmer 02; Flower+06

$H_3^+ + HD \longrightarrow H_2D^+ + H_2 + 230K$

If $n(H_2)$ is high, and T is low

$H_2D^+ + N_2 \rightarrow N_2D^+$ **Gas only**

$H_2D^+ + CN \rightarrow \ldots \rightarrow$ **DNC**

$H_2D^+ + NH_3 \rightarrow \ldots \rightarrow$ **NH_2D**

$H_2D^+ + H_2CO \rightarrow \ldots \rightarrow$ **HDCO**

GRAINS

Hasegawa et al. 1992; Roueff et al. 2007; Caselli & Ceccarelli 2012; Ceccarelli et al. 2012, PPVI

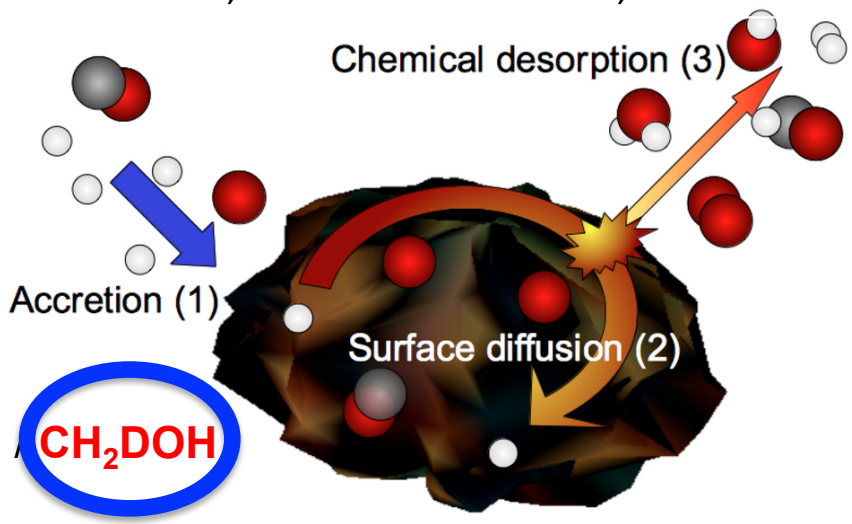
$O \rightarrow OH / OD \rightarrow H_2O$ / **HDO**

$C \rightarrow CH / CD \rightarrow \ldots \rightarrow CH_4$ / **CH_3D**

$N \rightarrow NH / ND \rightarrow \ldots \rightarrow NH_3$ / **NH_2D**

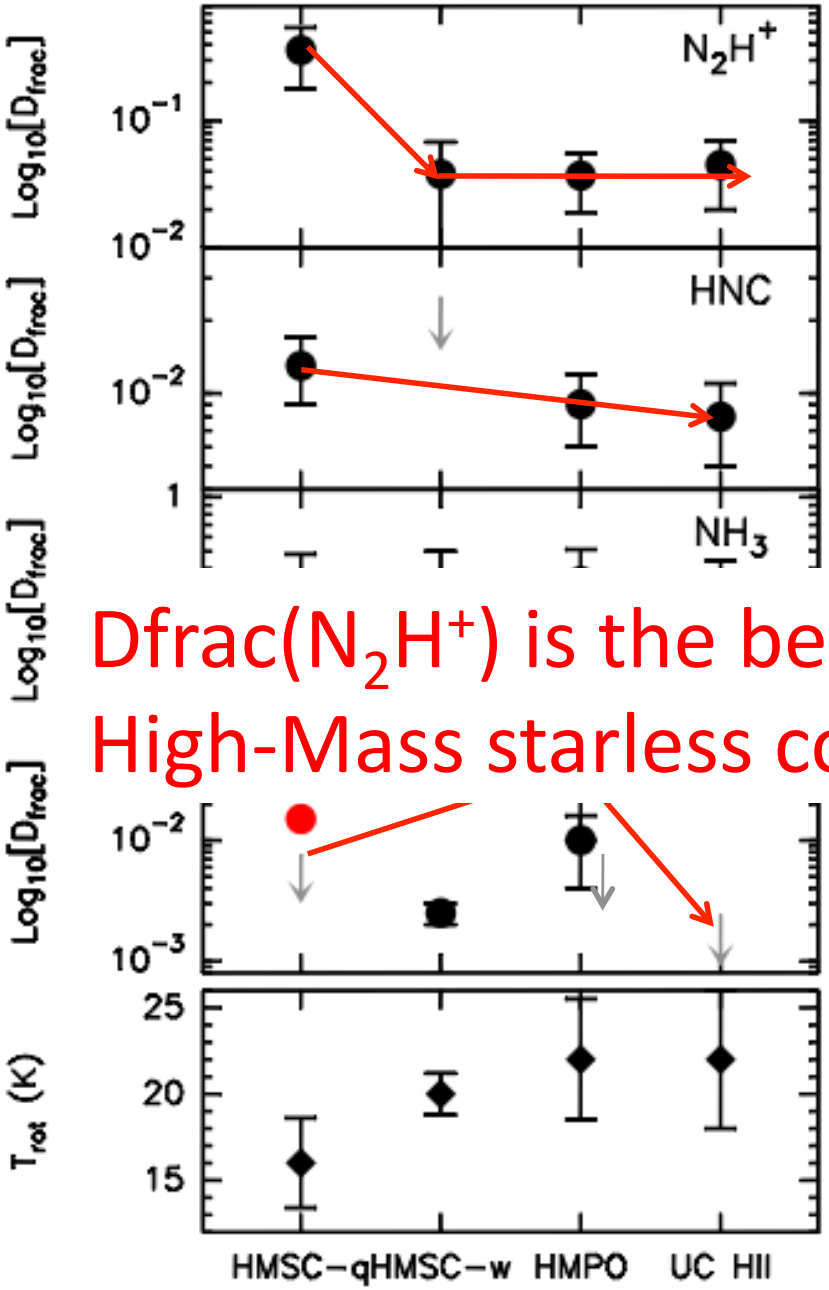
$CO \rightarrow HCO / DCO \rightarrow H_2CO$ / **HDCO** $\rightarrow \ldots \rightarrow CH_3OH$ / **CH_2DOH**

$CN \rightarrow HNC$ / **DNC**



Grains only

D-fractionation: the role of surface chemistry



Dfrac(N_2H^+): sharp decrease HMSC → HMPO

GAS

Dfrac(HNC): slight decrease HMSC → HMPO

Dfrac(N_2H^+) is the best (unique?) tool to identify High-Mass starless cores!

Dfrac(CH_3OH): increase (sharp?) HMSC →HMPO

GRAINS

Fontani et al. 2015, A&A

Formation of ^{15}N-molecules

e.g. Terzieva & Herbst 2000; Charnley & Rodgers 2002; Rodgers & Charnley 2008; Hily-Blant et al. 2013; Roueff et al. 2015

If T is low

$^{15}N + N_2H^+ \longrightarrow {}^{15}NNH^+ + N + 36K$

$N^{15}NH^+ + N + 28K$

$^{15}N + HCNH^+ \longrightarrow HC^{15}NH^+ + N + 36K$

Wirstroem et al. 2012

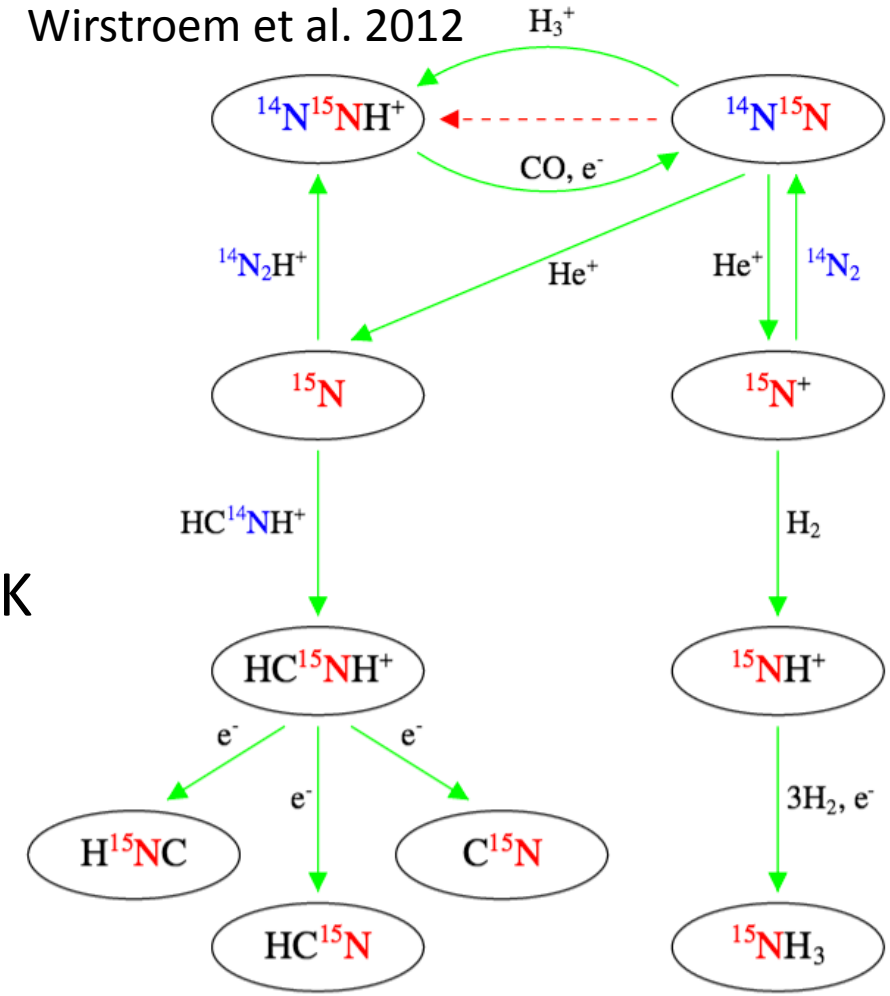
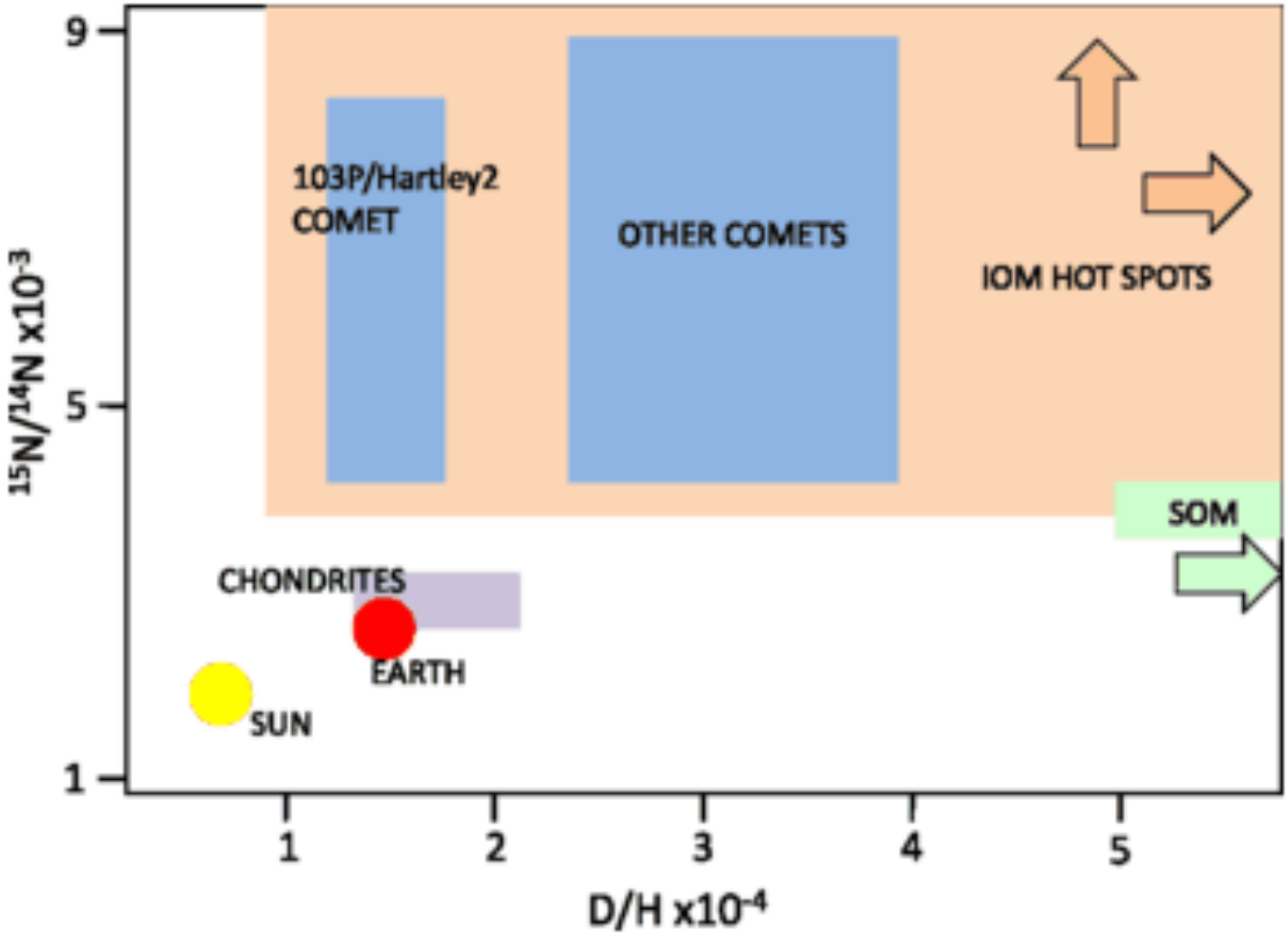


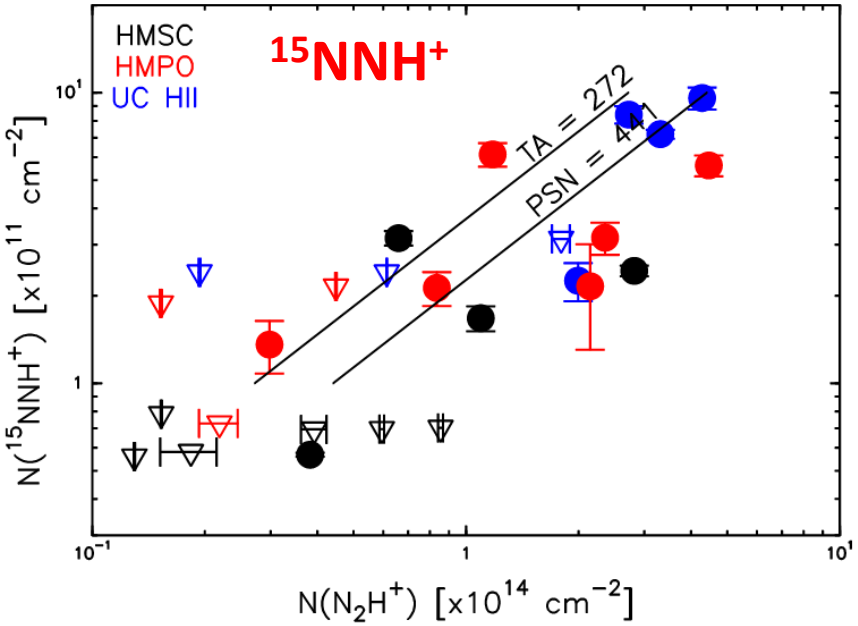
Figure 1. Chemical network showing the main reactions responsible for ^{15}N enhancement in nitriles and ammonia.

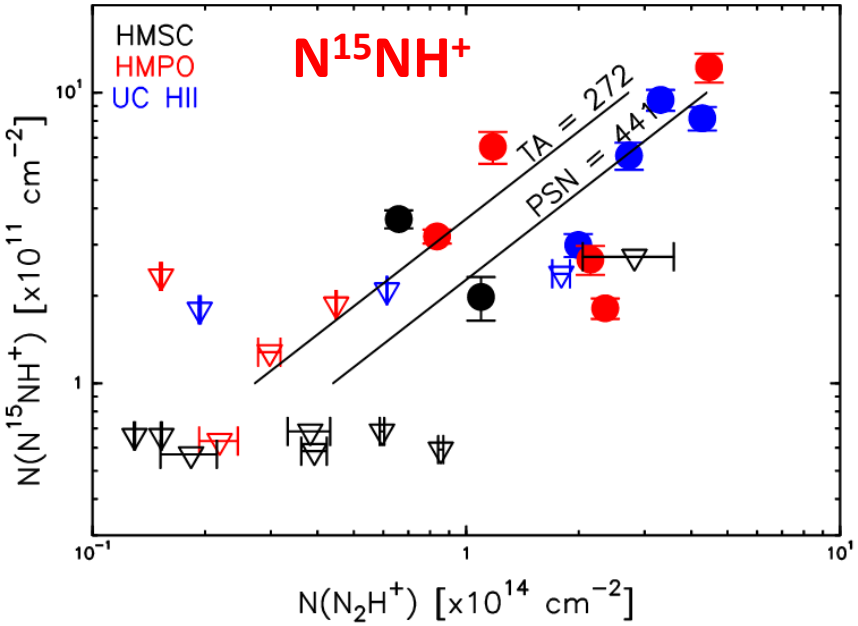
H and N isotopic anomalies

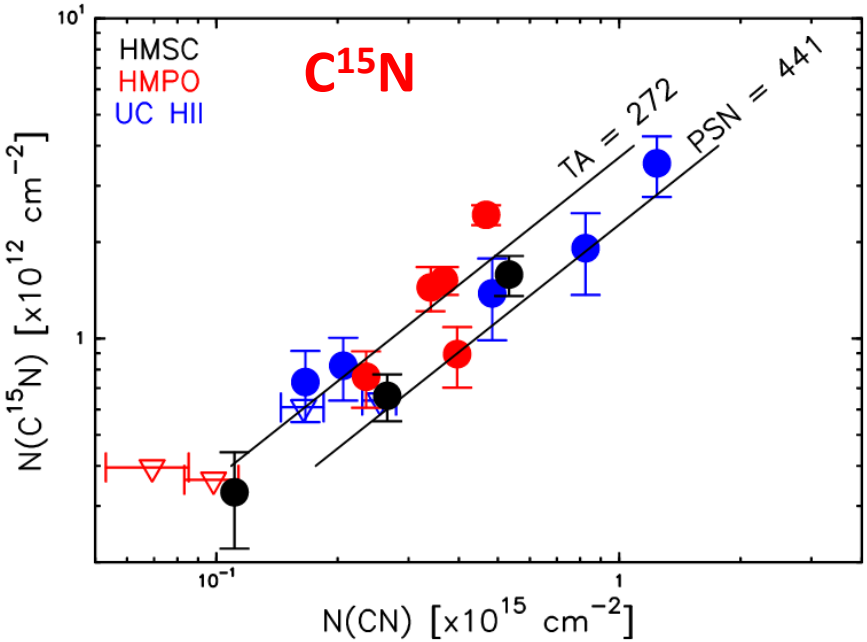
Caselli & Ceccarelli 2012, A&Arv (and references therein)



^{15}N fractionation in massive cores: N_2H^+ and CN







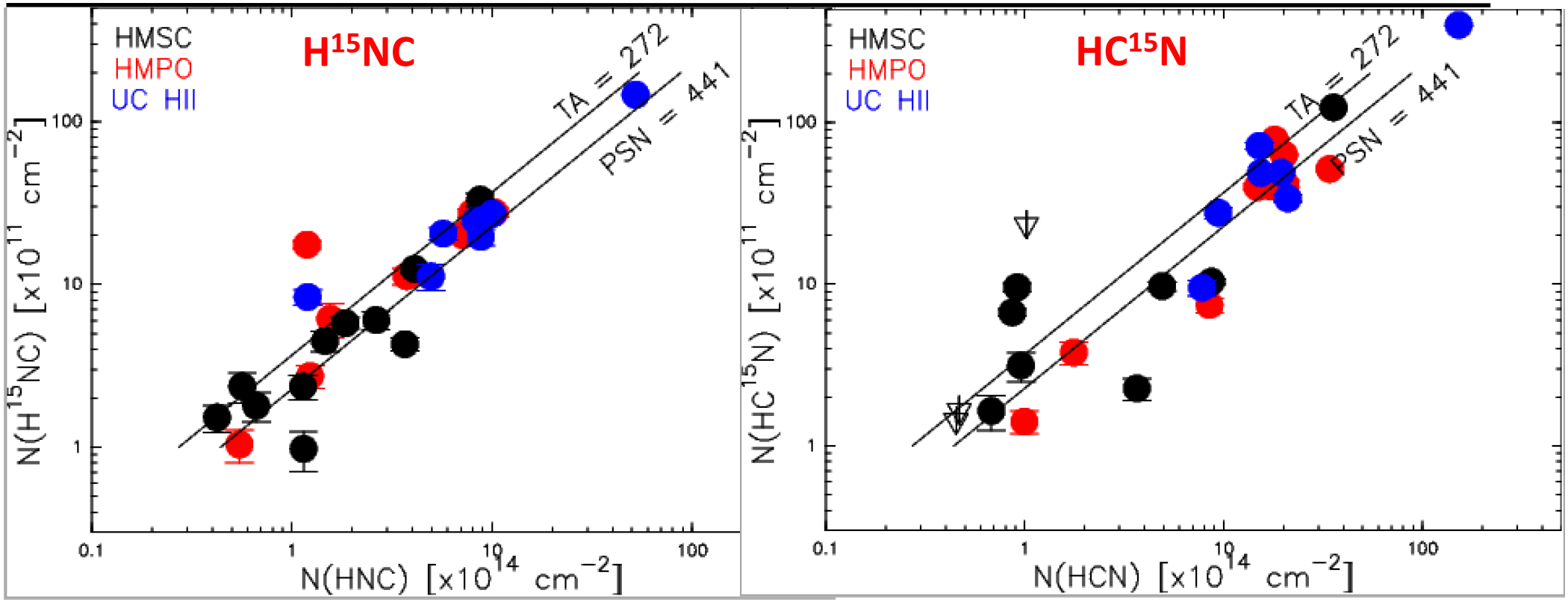
Fontani et al., ApJL, 808, 46

Main results:

1) ***Huge range of $^{14}N/^{15}N$ in N_2H^+***

2) NO statistical separation between the evolutionary groups
   → ***time does not seem to play a role in 15N fractionation***

^{15}N fractionation in massive cores: HN(13)C and H(13)CN



Colzi et al., in prep.

***PRELIMINARY* immediate results:**

1) ***Smaller spread of ^{14}N/^{15}N in HCN***

2) NO statistical separation between the evolutionary groups
→ ***time does not seem to play a role in 15N fractionation even in HCN and HNC***

Summary & conclusions

1) D-fractionation is favoured in cold and dense environments.

2) Observations of D-molecules match the theoretical expectations (overall)

3) ^{15}N-fractionation is still mysterious… but it does not seem to depend on core evolution

Recommended reading

- Herbst & Klemperer 1973, ApJ, 185, 505
- Duley & Williams, “Interstellar chemistry” ed. Academic Press
- Wilson & Rood 1994, ARA&A, 32, 191
- Flower et al. 2006, A&A, 449, 621
- Caselli & Ceccarelli 2012, A&ARv, 20, 56
- Ceccarelli et al. 2014, PPVI, 859

CO depletion

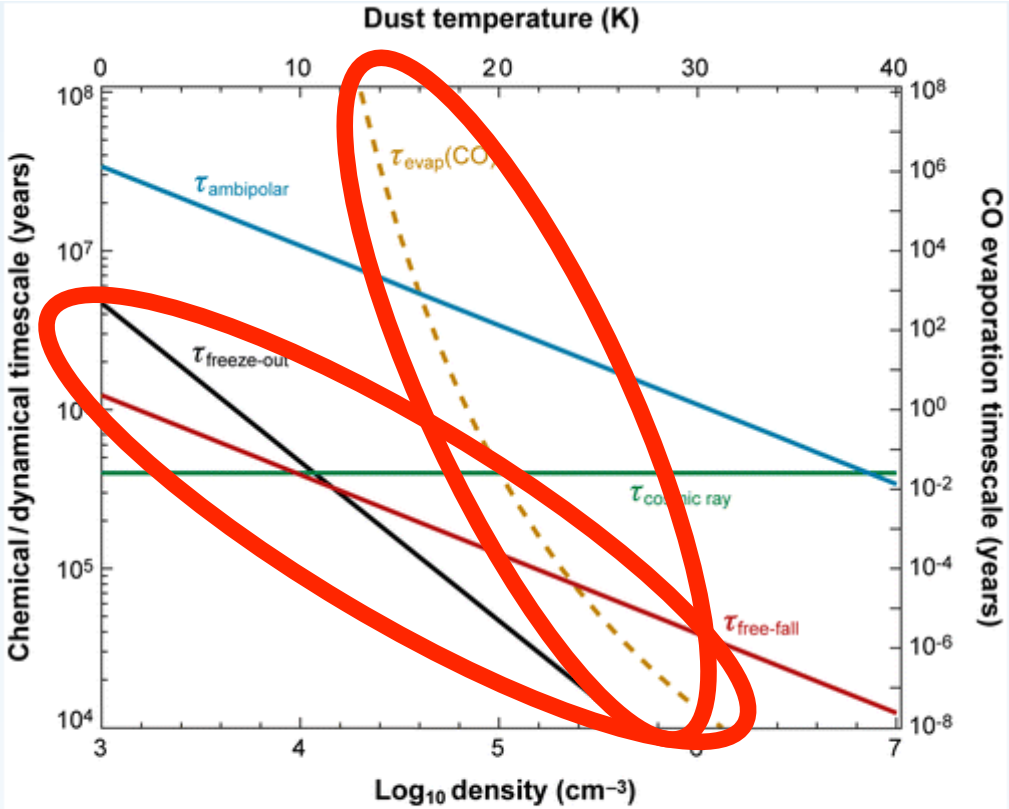
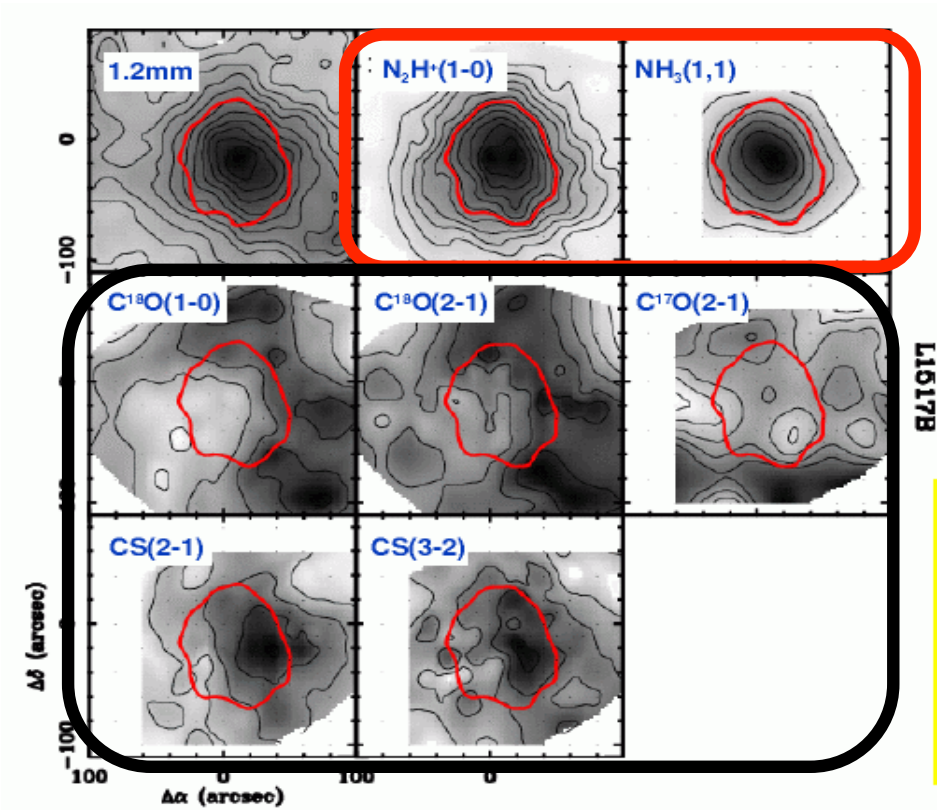
Caselli+99;+02; Tafalla+04; Hernandez+12; Fontani+12

T < 20 K

$n(H_2) > 10^5\ cm^{-3}$

High CO (and CS) DEPLETION FACTOR

$f_D = X(CO)^T/X(CO)^O > 1$



Bergin EA, Tafalla M. 2007.
Annu. Rev. Astron. Astrophys. 45:339–96