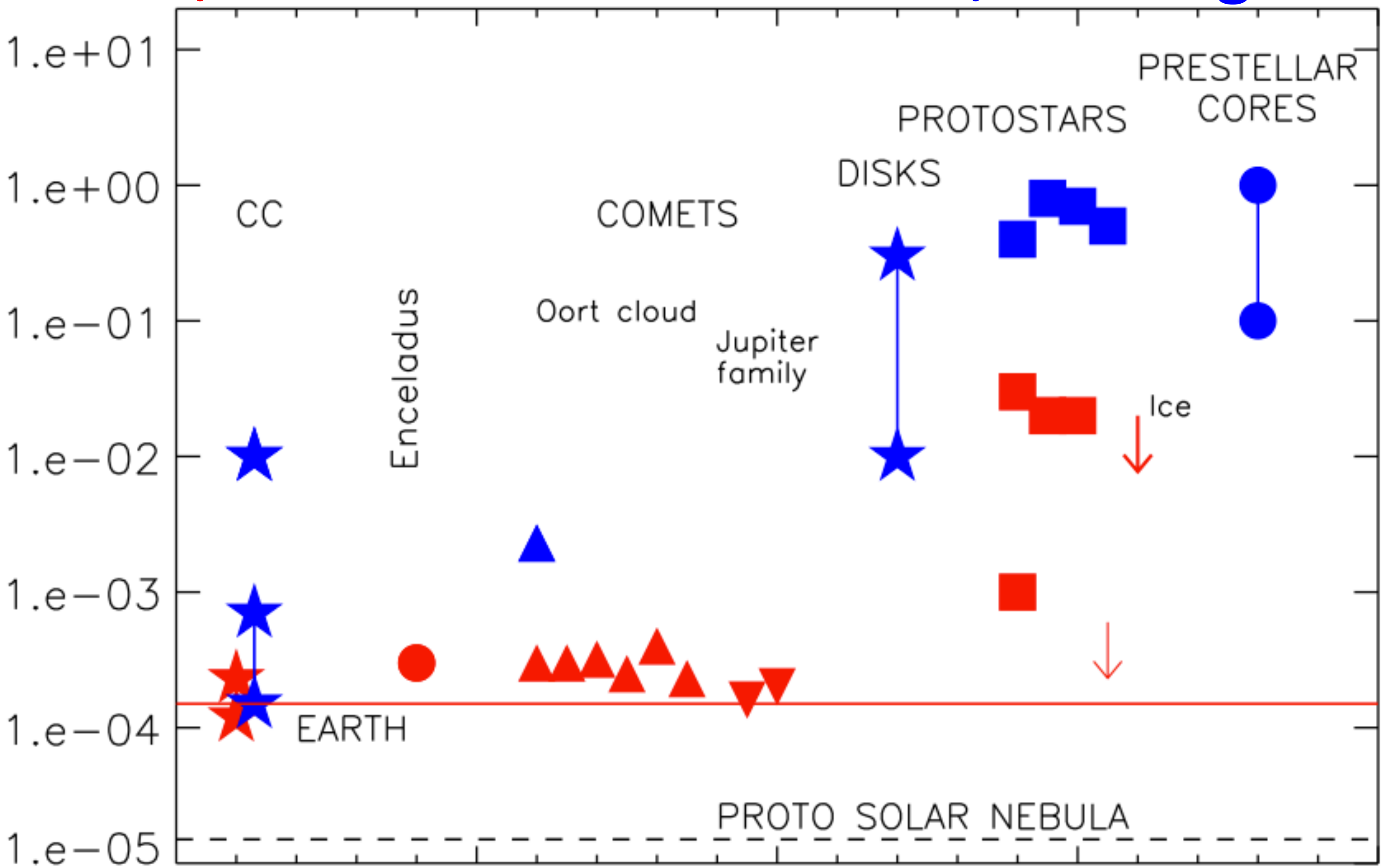
D and ^{15}N fractionation in pre-stellar cores

Paola Caselli
Center for Astrochemical Studies
Max-Planck-Institute for Extraterrestrial Physics


Deuterium fractionation

D/H in water

D/H in organics

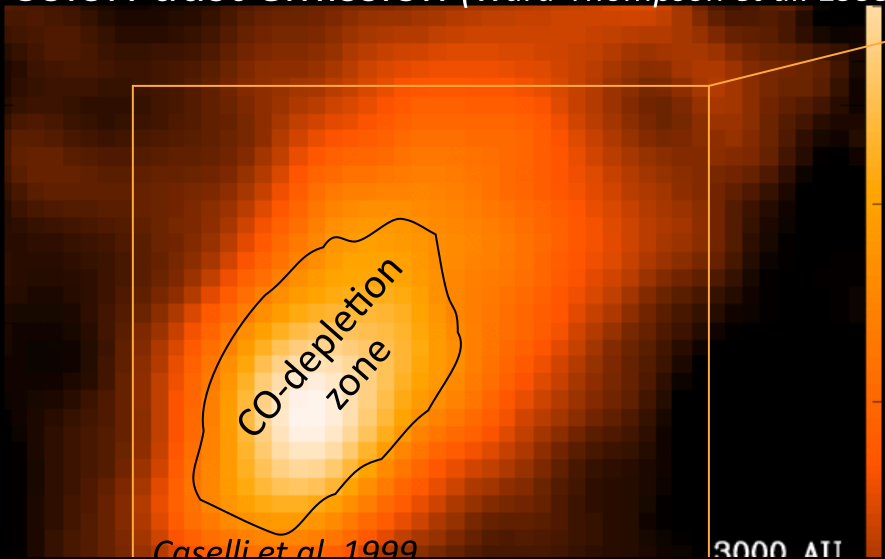


Ceccarelli, Caselli, Bocklelèe-Morvan, Mousis, Pizzarello, Robert, Semenov 2014, PPVI

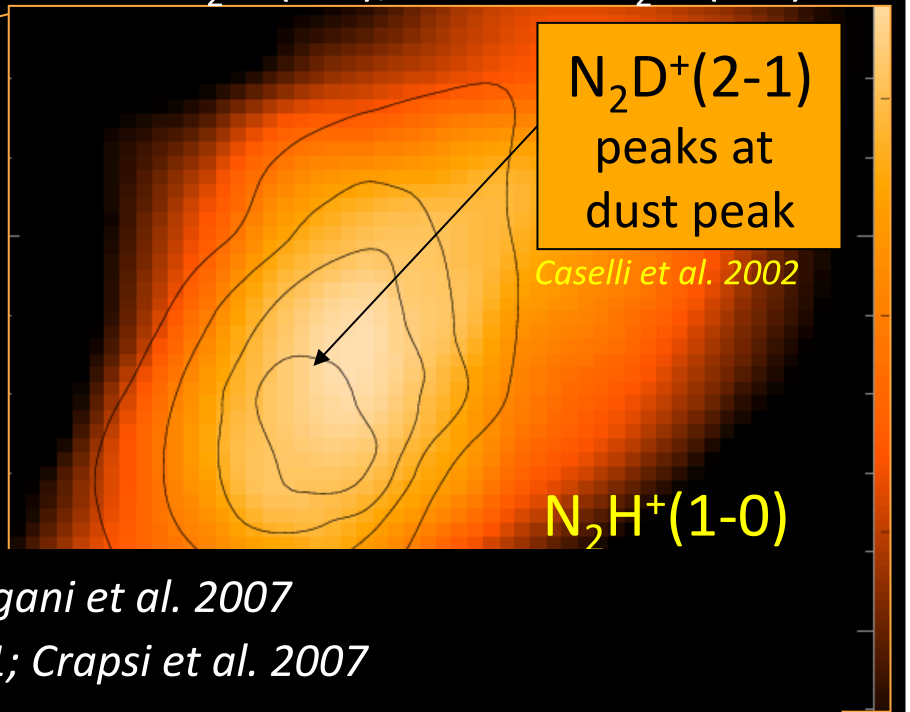
HDO/H2O in our Solar System requires ice production during the cold phase (Cleeves et al. 2014) ➔ pre-stellar phase is important !

Pre-stellar cores: freeze-out & deuterium fractionation

Color: dust emission *(Ward-Thompson et al. 1999)*



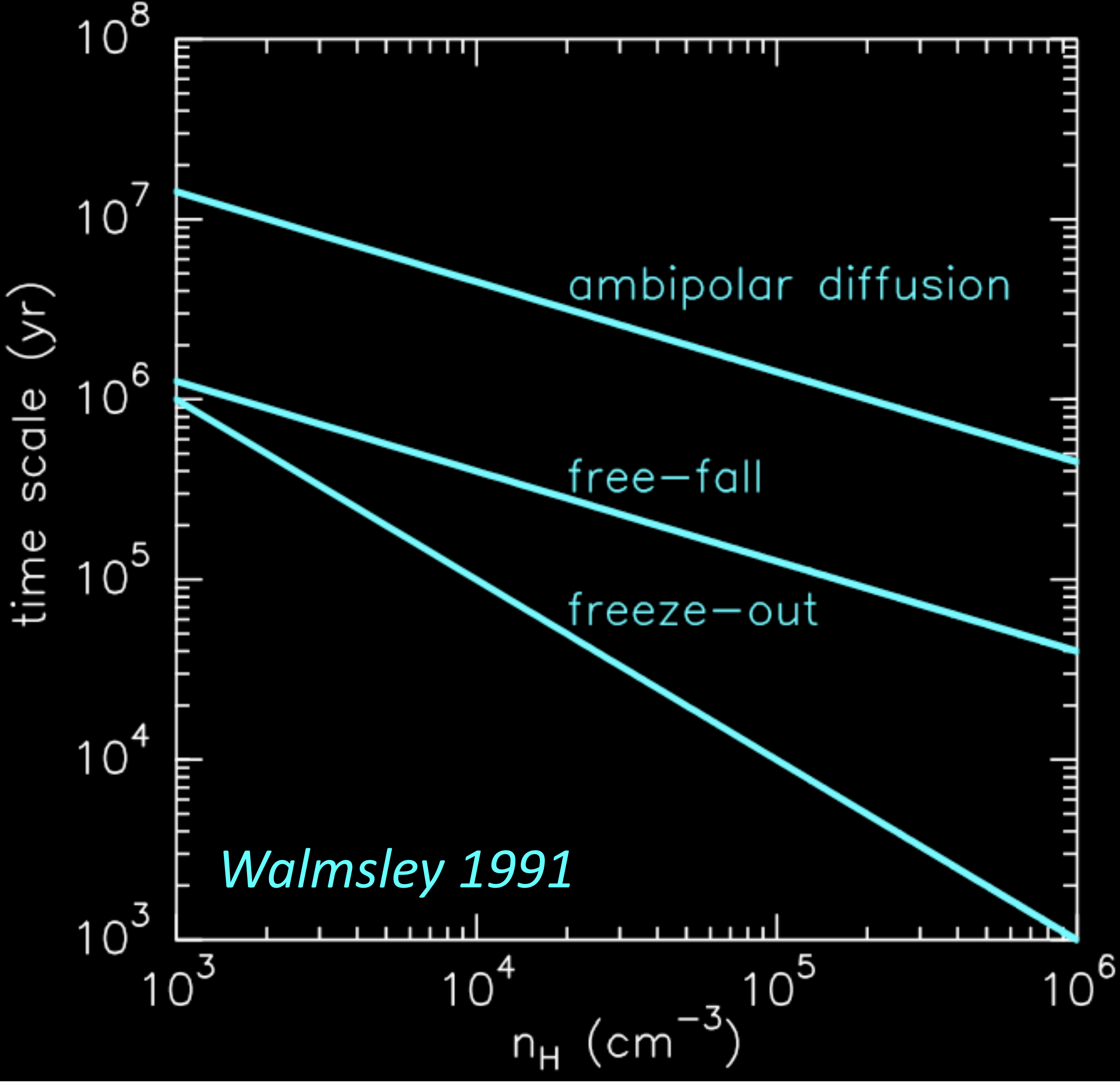
Color: N_2H^+(1-0); contour: N_2D^+(2-1)



N_2D^+/N_2H^+ ~ 0.03-0.7	*Crapsi et al. 2005; Pagani et al. 2007*
NH_2D/NH_3 ~ 0.06-0.4	*Shah & Wootten 2001; Crapsi et al. 2007*
D_2CO/H_2CO ~ 0.01-0.1	*Bacmann et al. 2003*
CH_2DOH/CH_3OH ~0.1	*Bizzocchi et al. 2014*
DCN/HCN ~ 0.01-0.04	*Turner 2001*
DNC/HNC ~ 0.02-0.09	*Hirota et al. 2003*
DCO^+/HCO^+ ~ 0.04	*Butner et al. 1995; Caselli et al. 2002*
$c\text{-}C_3D_2/c\text{-}C_3H_2$ ~ 0.01-0.02	*Spezzano et al. 2013*

+ see talk of Anna Punanova

Dynamical & Chemical Timescales



$$t_{ambipolar} \approx 2.5 \times 10^{13}\, x(e)\ \mathrm{yr}$$
$$\approx 4.5 \times 10^{8} / \sqrt{n_H}\ \mathrm{yr}$$

$$t_{free-fall} = \sqrt{\frac{3\pi}{32G\rho}}$$
$$\approx 4 \times 10^{7} / \sqrt{n_H}\ \mathrm{yr}$$

$$t_{freeze-out} = \frac{1}{\alpha n_d \pi a_d^2 \mathrm{v}_t}$$
$$\approx 10^{9} / n_H\ \mathrm{yr}$$

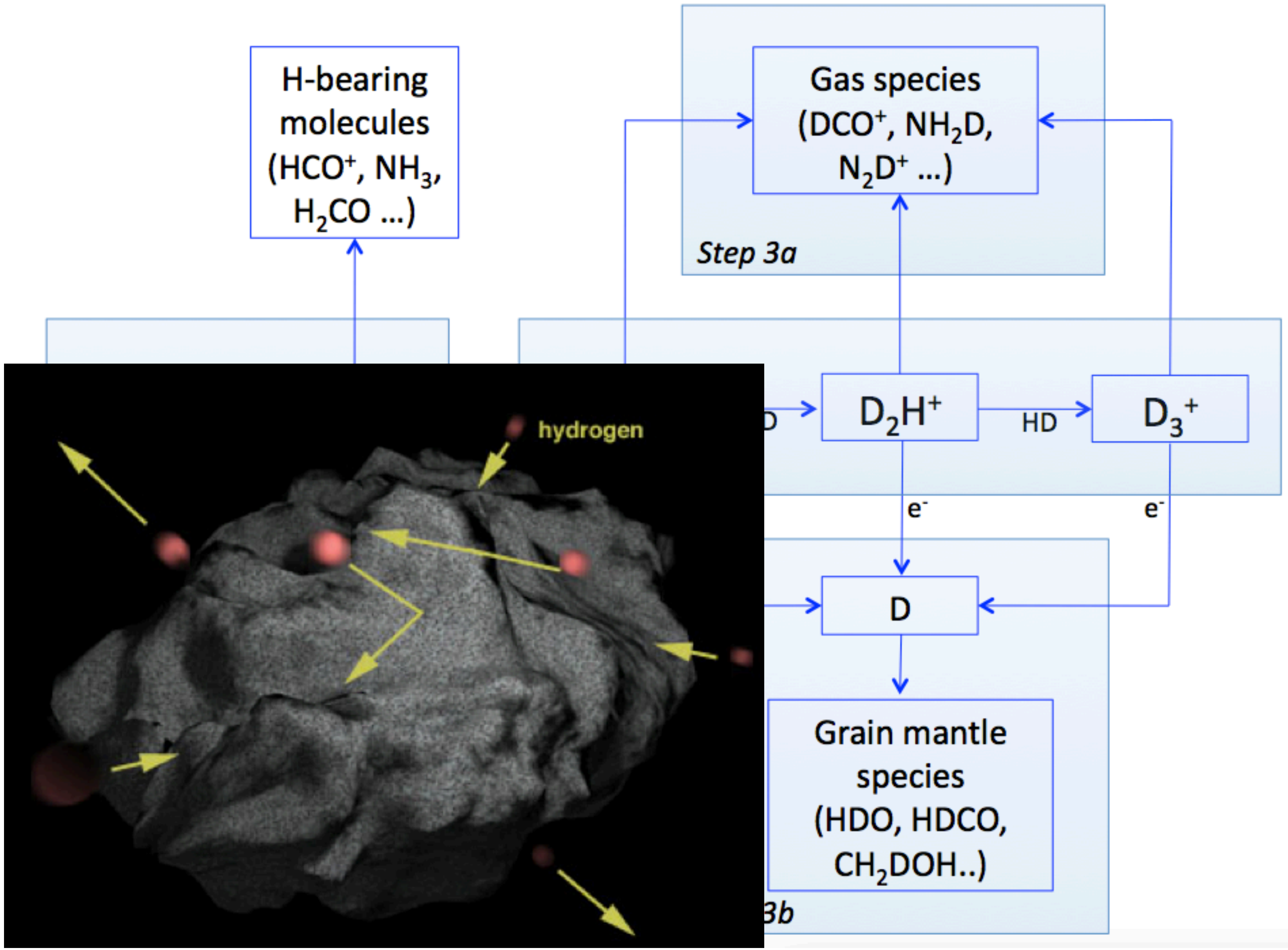
Deuterium Fractionation at T < 20 K

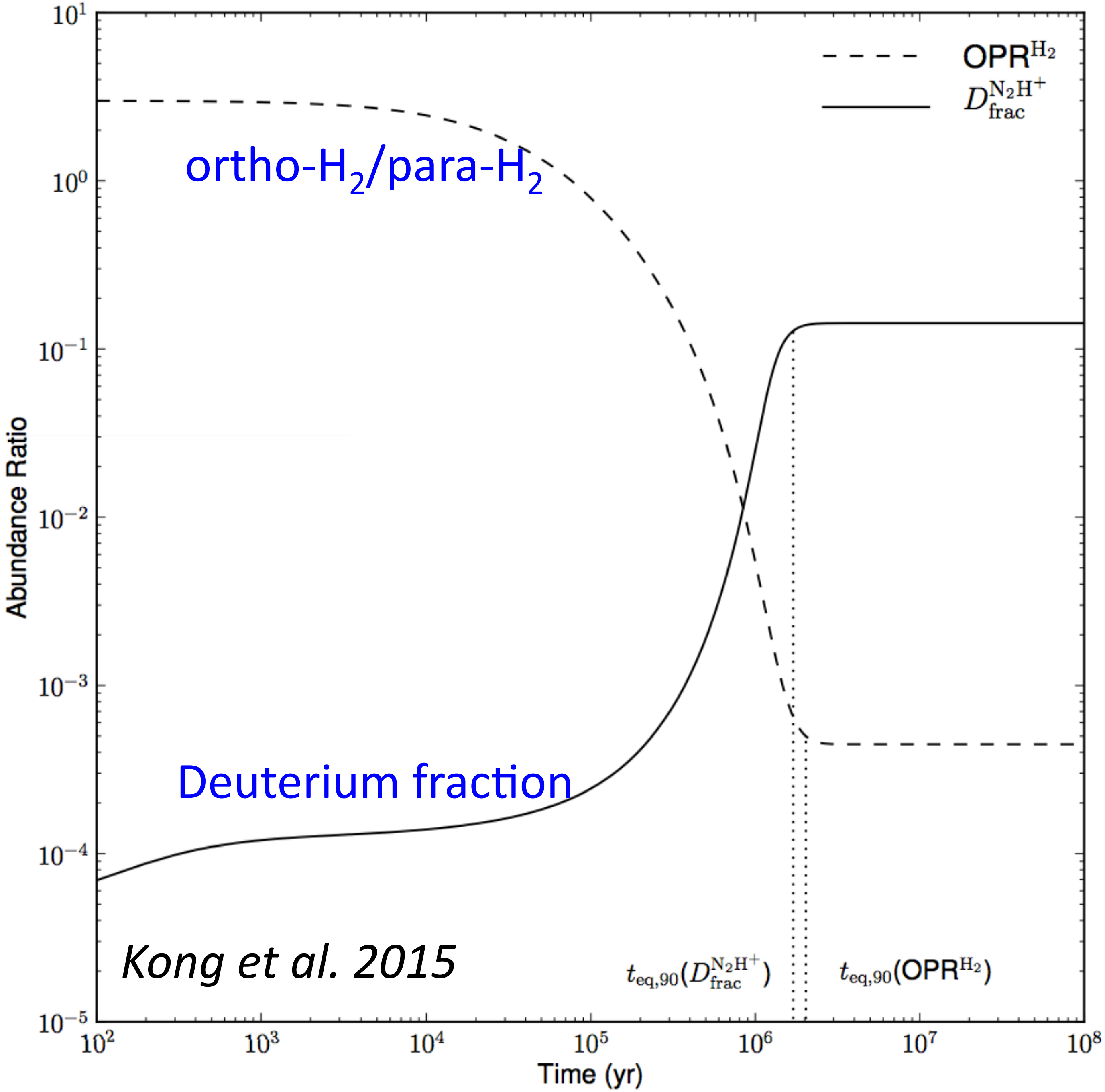
$$H_3^+ + HD \rightarrow H_2D^+ + H_2 + 230\ K$$ *(Watson 1974)*

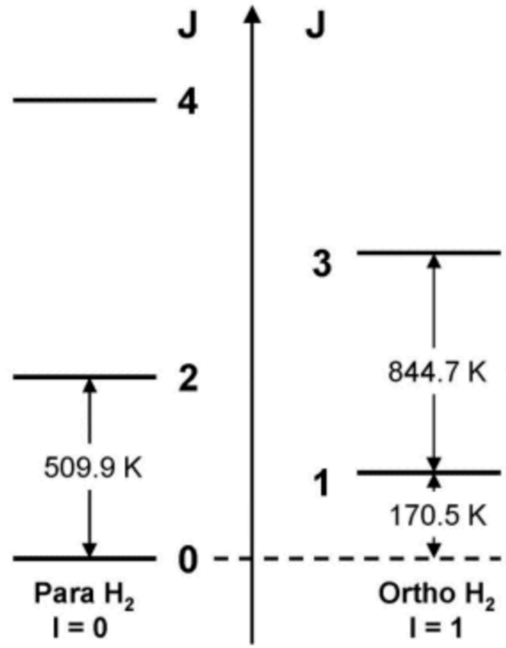
H_2D^+ / H_3^+ increases if the abundance of gas phase neutral species decreases *(Dalgarno & Lepp 1984)*:

LOWER H_2D^+ and H_3^+ destruction rates	+	HIGHER H_2D^+ formation rate	=	LARGER H_2D^+/H_3^+ abundance ratio and deuterium fractionation

$$H_2D^+ + CO \rightarrow DCO^+ + H_2$$
$$H_2D^+ + N_2 \rightarrow N_2D^+ + H_2$$


H-bearing molecules (HCO+, NH3, H2CO ...)
Gas species (DCO+, NH2D, N2D+ ...)
Step 3a
hydrogen
D2H+
HD
D3+
e-
e-
D
Grain mantle species (HDO, HDCO, CH2DOH..)
3b





H_3^+ + HD → H_2D^+ + p-H_2

H_3^+ + HD ← H_2D^+ + o-H_2

Pagani et al. 1992
Gerlich et al. 2002
Walmsley et al. 2004

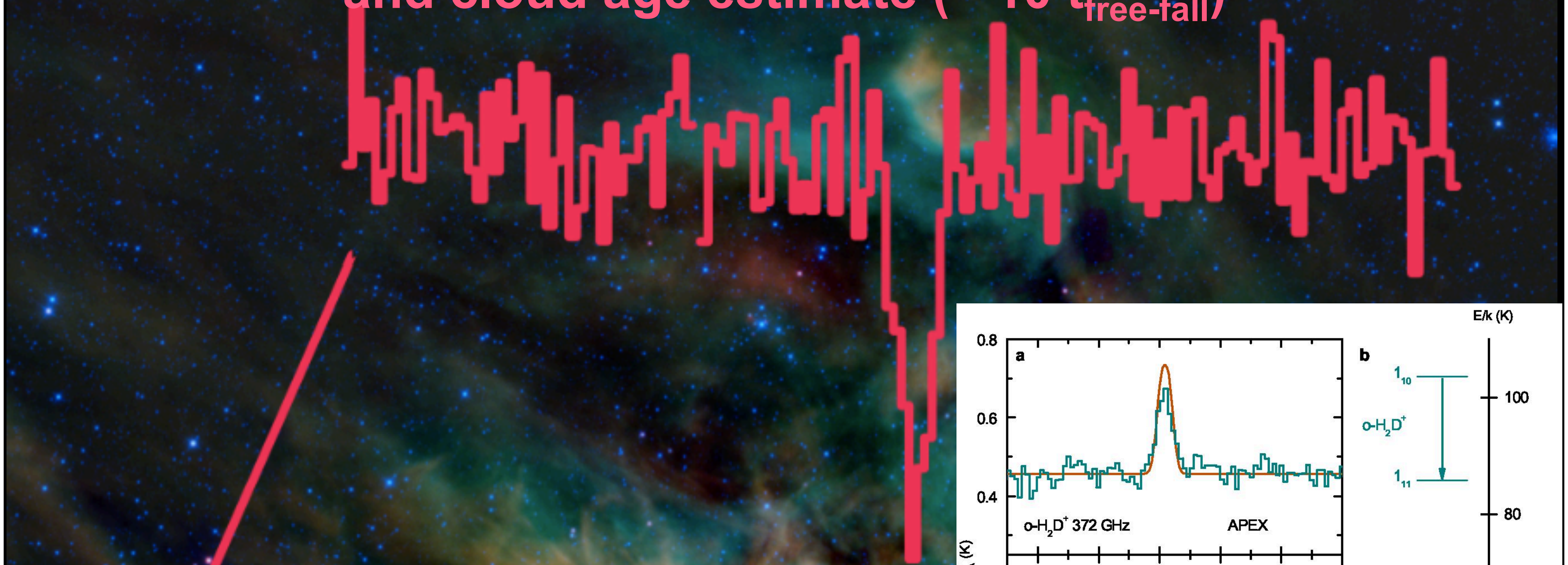
Analytical relation between the H_2 and H_2D^+ ortho-to-para ratios

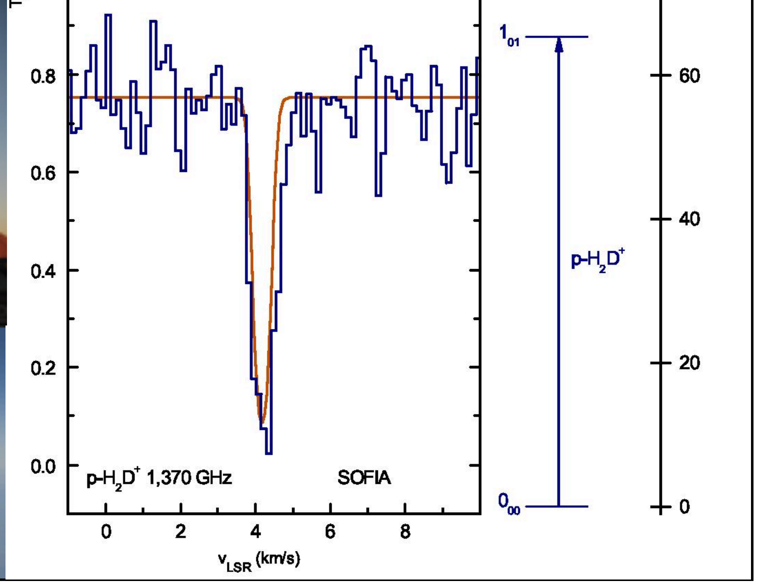
$$p\text{-}H_2D^+ + o\text{-}H_2 \overset{k_1}{\Leftrightarrow} o\text{-}H_2D^+ + p\text{-}H_2$$
$$o\text{-}H_2D^+ + o\text{-}H_2 \overset{k_2}{\Leftrightarrow} p\text{-}H_2D^+ + p\text{-}H_2$$
$$o\text{-}H_2D^+ + o\text{-}H_2 \overset{k_3}{\Leftrightarrow} p\text{-}H_2D^+ + o\text{-}H_2$$

$$\frac{[o\text{-}H_2D^+]}{[p\text{-}H_2D^+]} = \frac{(k_1^+ + k_3^-) \times [o\text{-}H_2]/[p\text{-}H_2] + k_2^-}{(k_2^+ + k_3^+) \times [o\text{-}H_2]/[p\text{-}H_2] + k_1^-}$$

Hugo et al. 2009

FIRST DETECTION OF para-H2D+ TOWARD IRAS16293-2422 and cloud age estimate (~ 10 $t_{free\text{-}fall}$)





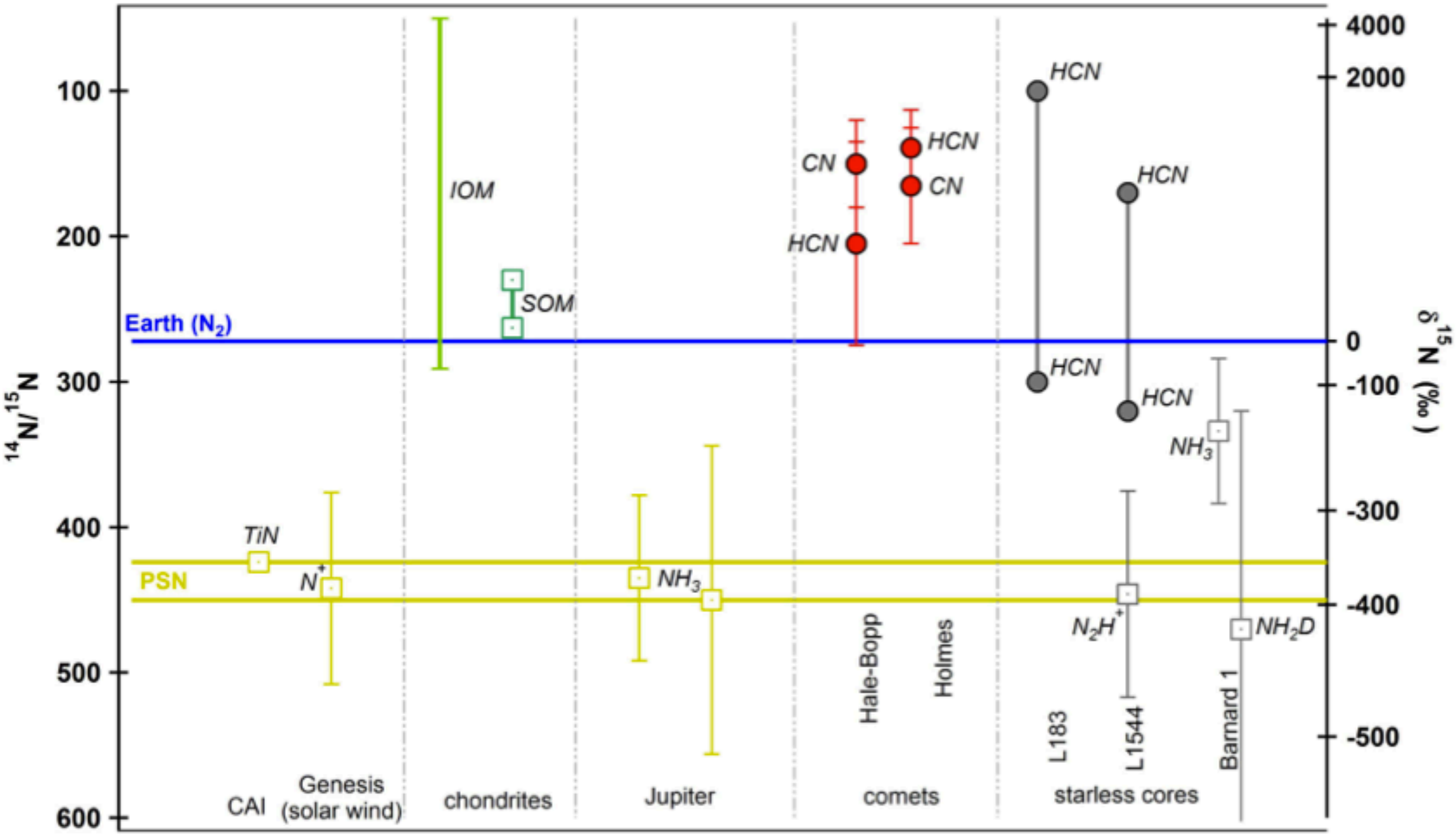
Brünken et al. 2014, Nature

ALMA is unveiling the central 1000 AU of prestellar cores: fragmentation and large CO freeze out.

Caselli et al., submitted – Pineda et al., in prep.
(see also H_2D^+ detection by Friesen et al. 2014)
For D-fractionation in massive cores: see Jonathan Tan's talk

^{15}N fractionation

Differential ^{15}N enhancement between nitrile- and amine-bearing interstellar molecules. No correlation with D-frac.



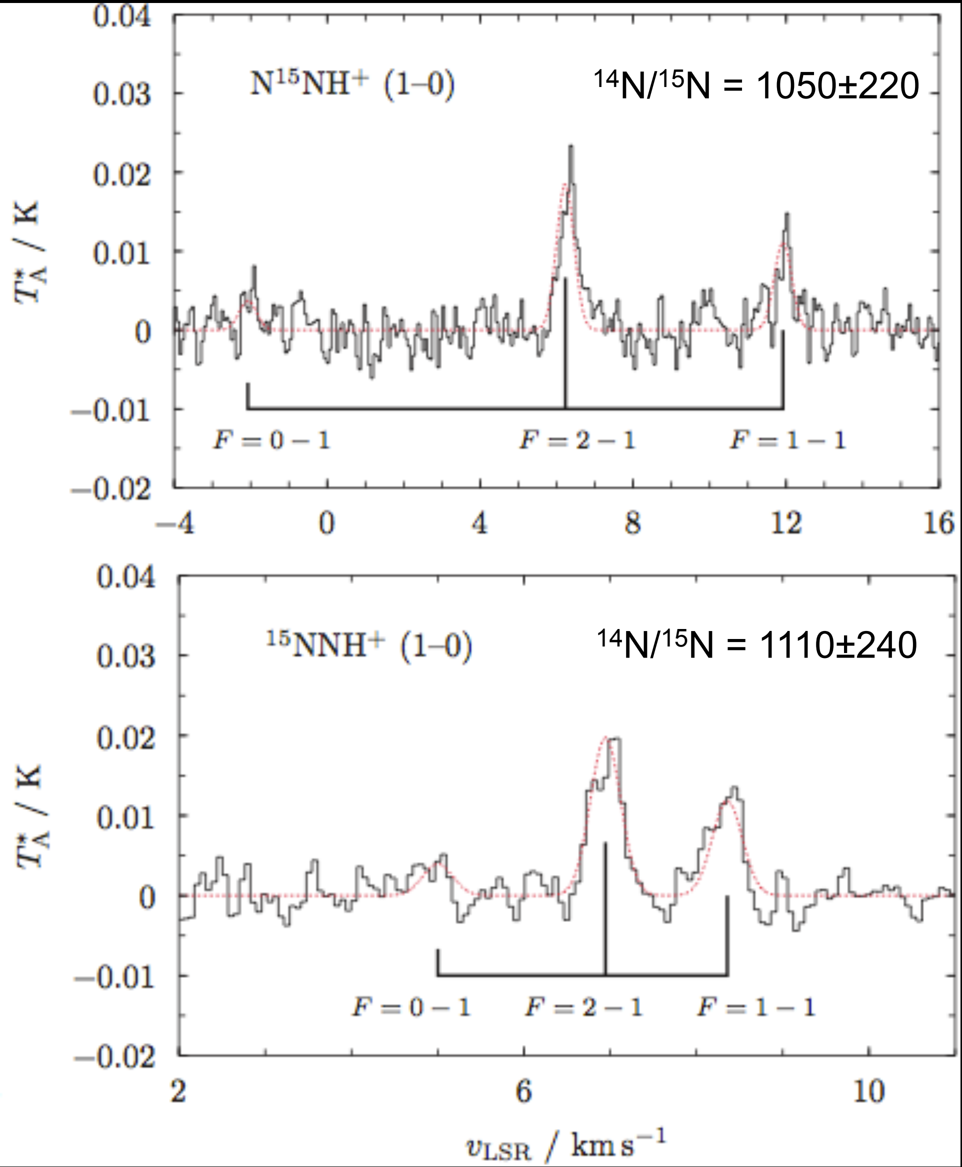
***Hily-Blant et al. 2013**; Bizzocchi et al. 2013; Wampfler et al. 2014; Fontani et al. 2015*

The $^{14}N/^{15}N$ ratio

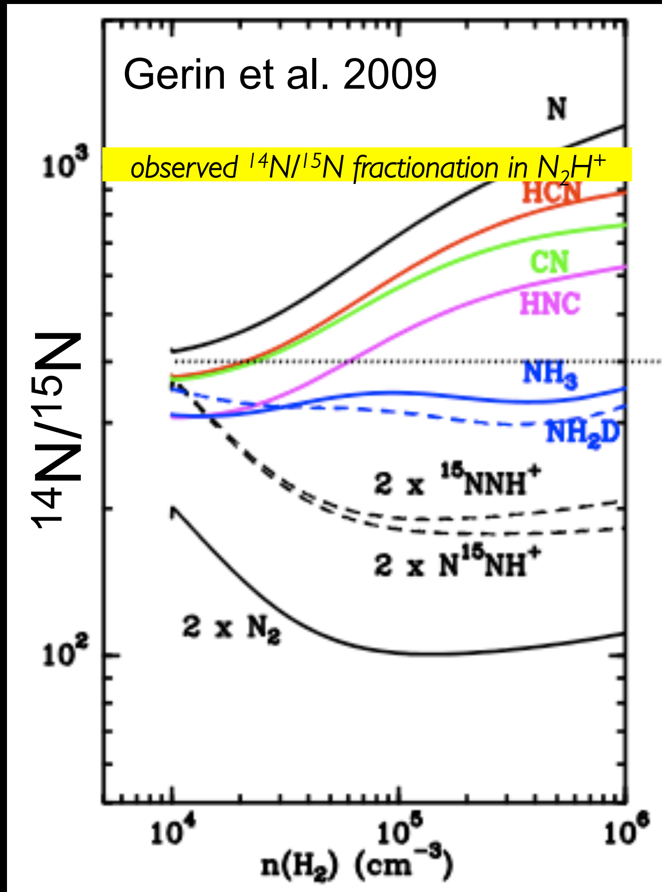
Large ^{15}N excess is found in primitive material (meteorites, IDPs, cometary dust particles returned by *Stardust*): e.g. $^{14}N/^{15}N \sim 65$ found in the "hot spots" of the meteorite Bells (*Buseman et al. 2006*).

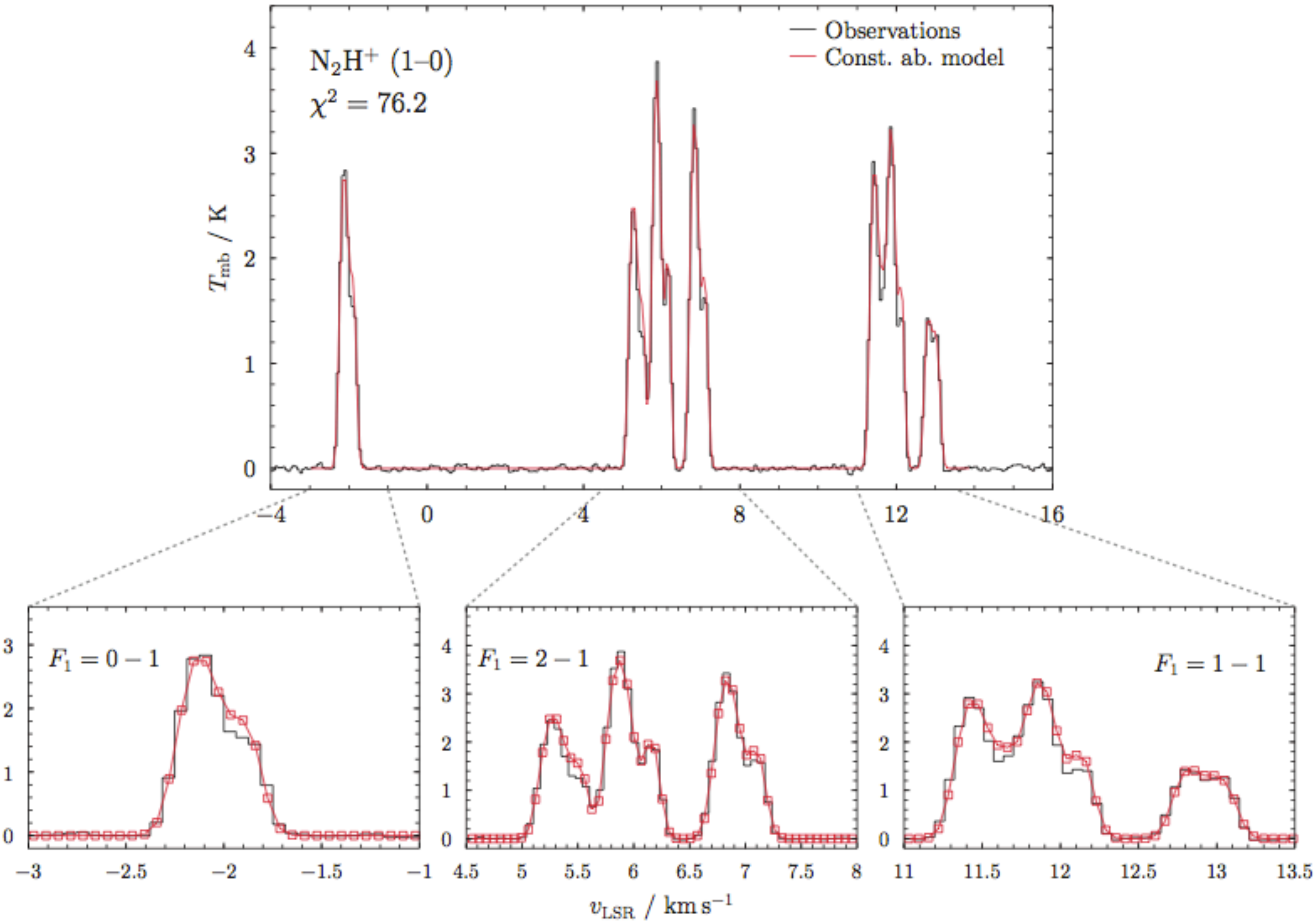
D-enriched spots do not always coincide with ^{15}N-enriched ones *(e.g. Buseman et al. 2010; Robert et al. 2006)*.

^{15}N-fractionation in N_2H^+ *(Bizzocchi et al. 2010, 2013)*



$^{14}N/^{15}N$ in pre-stellar core higher than protosolar value! – disagreement with chemical models.

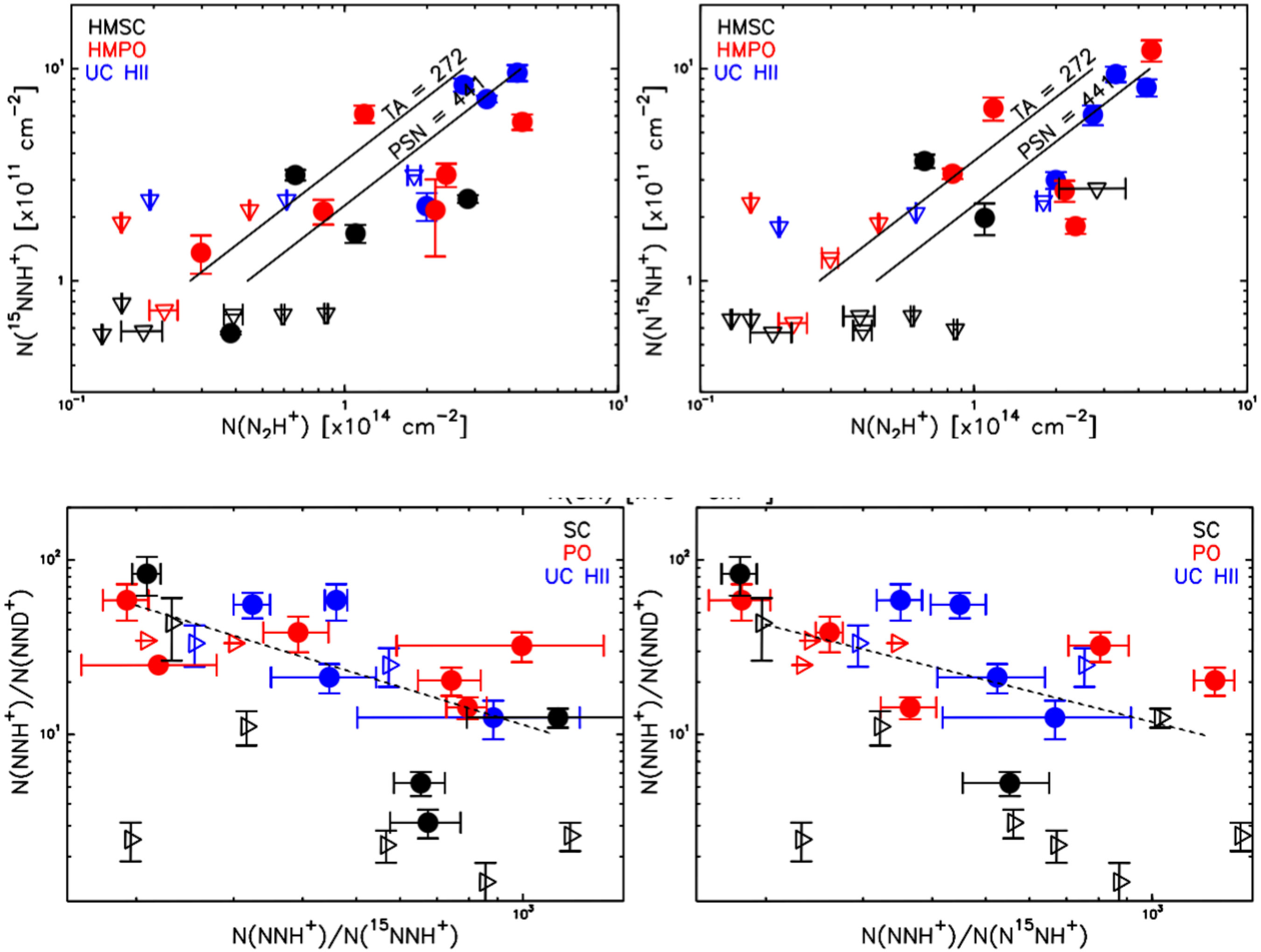




Bizzocchi et al. 2013

$^{15}NNH^+$ and $N^{15}NH^+$ in high-mass star forming regions

Fontani et al. 2015 *(+ see poster by Laura Colzi !)*



$180 < {}^{14}N/{}^{15}N < 1300$ with N_2H^+ -- $270 < {}^{14}N/{}^{15}N < 440$ with CN

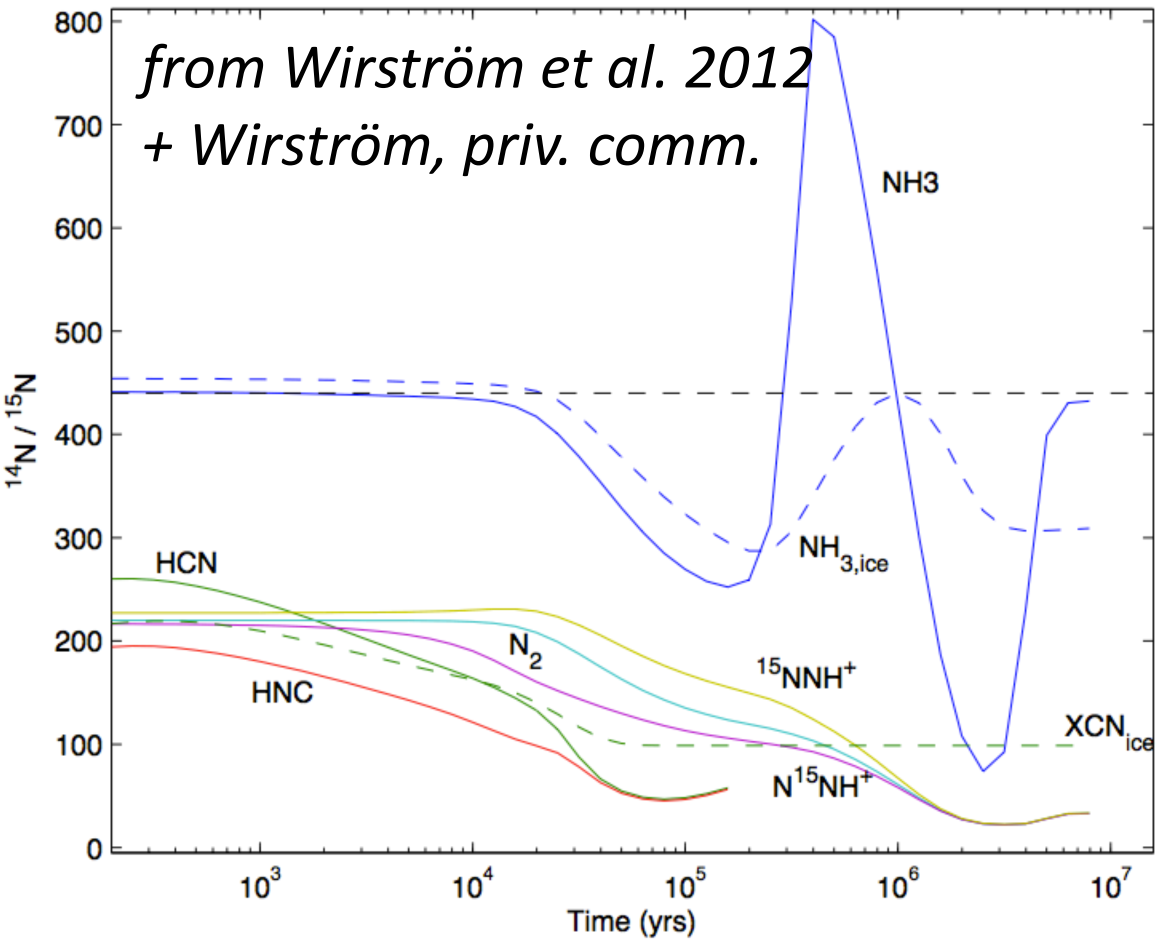
Freeze-out effect on ^{15}N fractionation

Under normal interstellar conditions, ^{14}N and ^{15}N are continuously exchanged within N_2 through the sequence:

$$N_2 \xrightarrow{He^+} N \xrightarrow{OH} NO \xrightarrow{N} N_2$$

But if freeze-out is large, there is insufficient OH to drive the above sequence and ^{15}N is preferentially incorporated into gas phase N_2 as well as into NH_3 → significant fractionation is expected.

Rodgers & Charnley 2008a,b



(i) No correlation with D-fractionation;

(ii) Fractionation in HCN and CN is ***faster*** (10^5 yr) than in NH_3 (~10^6 yr);

WHAT'S GOING ON?

Is $^{15}N^{14}N$ preferentially frozen onto dust grains ?

Is ^{15}N chemically depleted before N_2 and N_2H^+ formation?

Uncertain rate coefficients ?

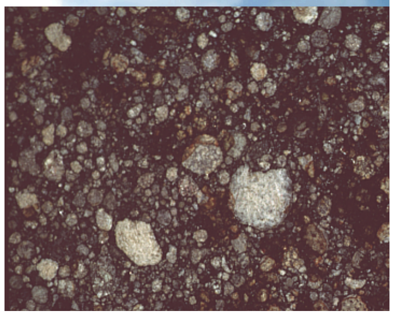
Overestimated molecular freeze-out ?

Ortho-to-para H_2…

CONCLUSIONS

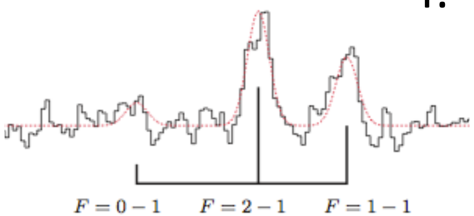
1. Pre-stellar cores are deuteration factories because of the low temperatures and high levels of molecular freeze-out (H_2D^+, D_2H^+, D_3^+, D).

2. Differential ^{15}N enhancement between nitrile- and amine-bearing interstellar molecules. Large ^{15}N fractionation in nitriles also found in comets.



3. No correlation of ^{15}N and D fractionation measured in pre-stellar cores and in meteoritic hot spots.

$^{15}NNH^+(1\text{-}0)$



4. ^{15}N – fraction in N_2H^+ is about two times less than the protosolar value ('anti-fractionation'): disagreement with chemical model prediction.