# Models of Nitrogen Fractionation in Depletion Cores

Eva Wirström
Department of Space, Earth and Environmental Sciences
Chalmers University of Technology, Sweden

Collaborators:
S. Charnley – NASA Goddard SFC
L. Bizzocchi – MPE, Garching
L. Dore – Università di Bologna

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# Why dark pre-stellar cores?

Example: Barnard 68
FORS Team, 8.2m VLT Antu, ESO

Cold: $T \approx 5 - 15$ K

Dense: $n(H_2) \sim$ 1e5-7 $cm^{-3}$

Dark: $A_v > 10$ mag

e.g. Crapsi et al (2005)

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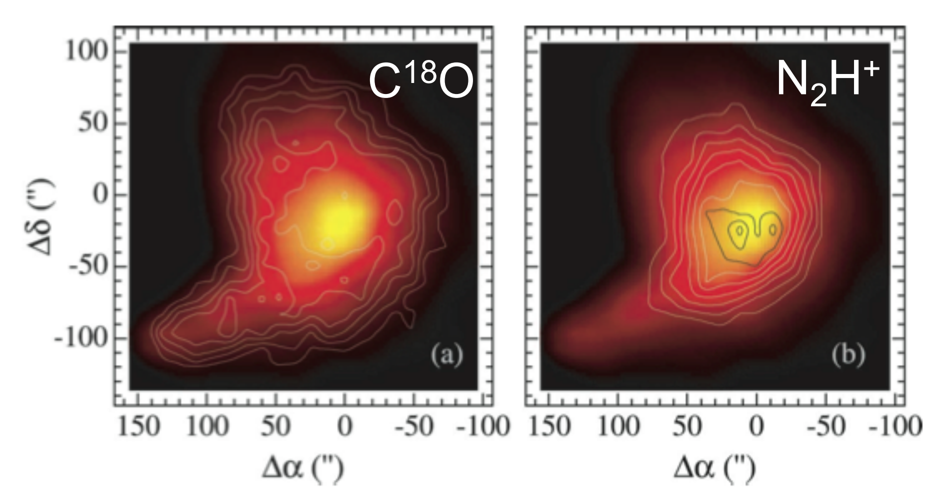
- $N_2$ ($N_2H^+$) still in gas
- High atomic D/H

e.g. Crapsi et al (2005)




B68, Bergin et al (2002)

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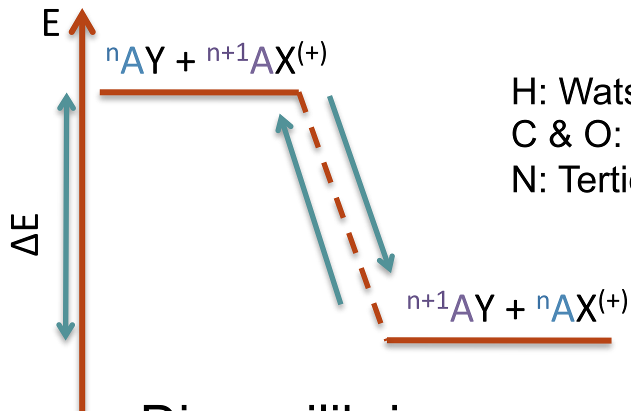
→ Disequilibrium chemistry

Gas-grain interaction

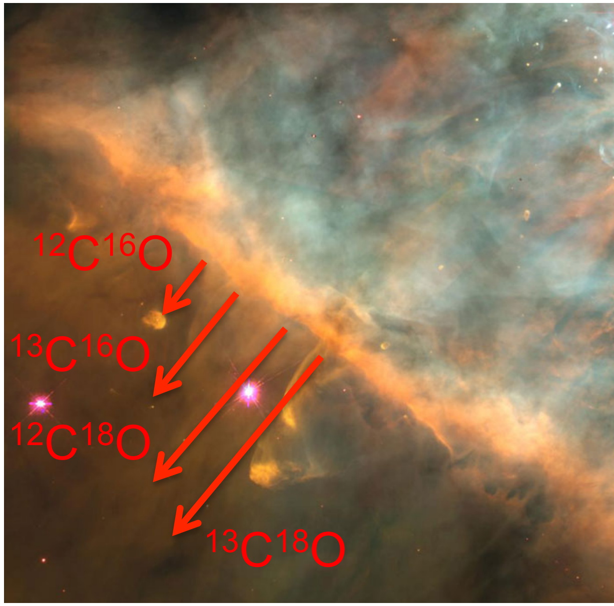
**Potential for most extreme $^{15}N$ (and D) enhancements (and depletions)**

# Isotope fractionation processes




H: Watson (1974), Herbst (1982)
C & O: Langer et al (1984)
N: Tertieva & Herbst (2000)

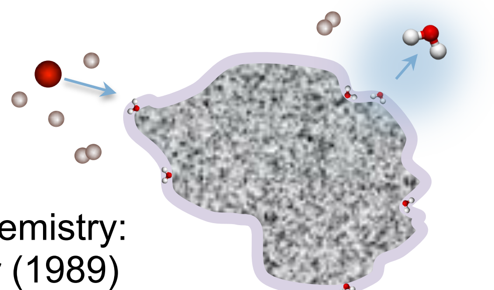
Disequilibrium gas-phase chemistry




Self-shielding against photodissociation

$H_2$: Watson (1973)
CO: van Dishoeck & Black (1988)
$N_2$: Heays et al. (2014)

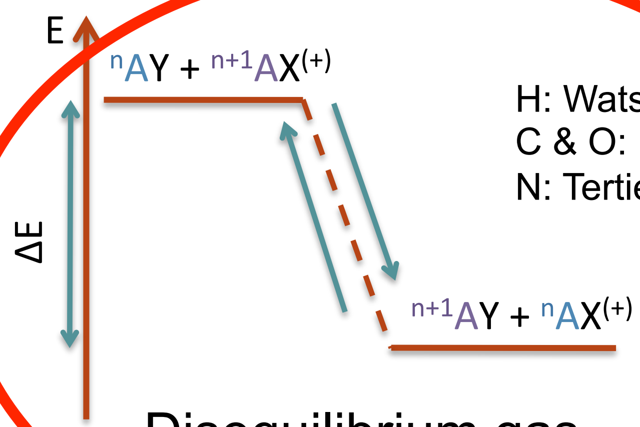
Gas-grain interaction



Surface/ice chemistry:
Brown & Millar (1989)

Mass dependence:
Young & Schauble (2011);
Smith et al. (2013)

# Isotope fractionation processes

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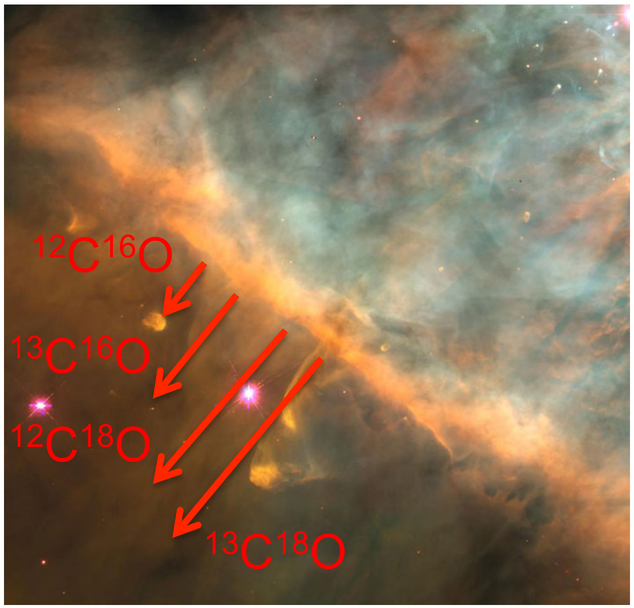


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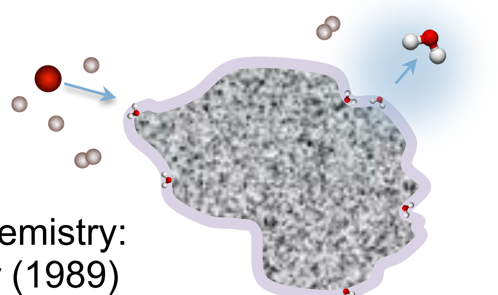

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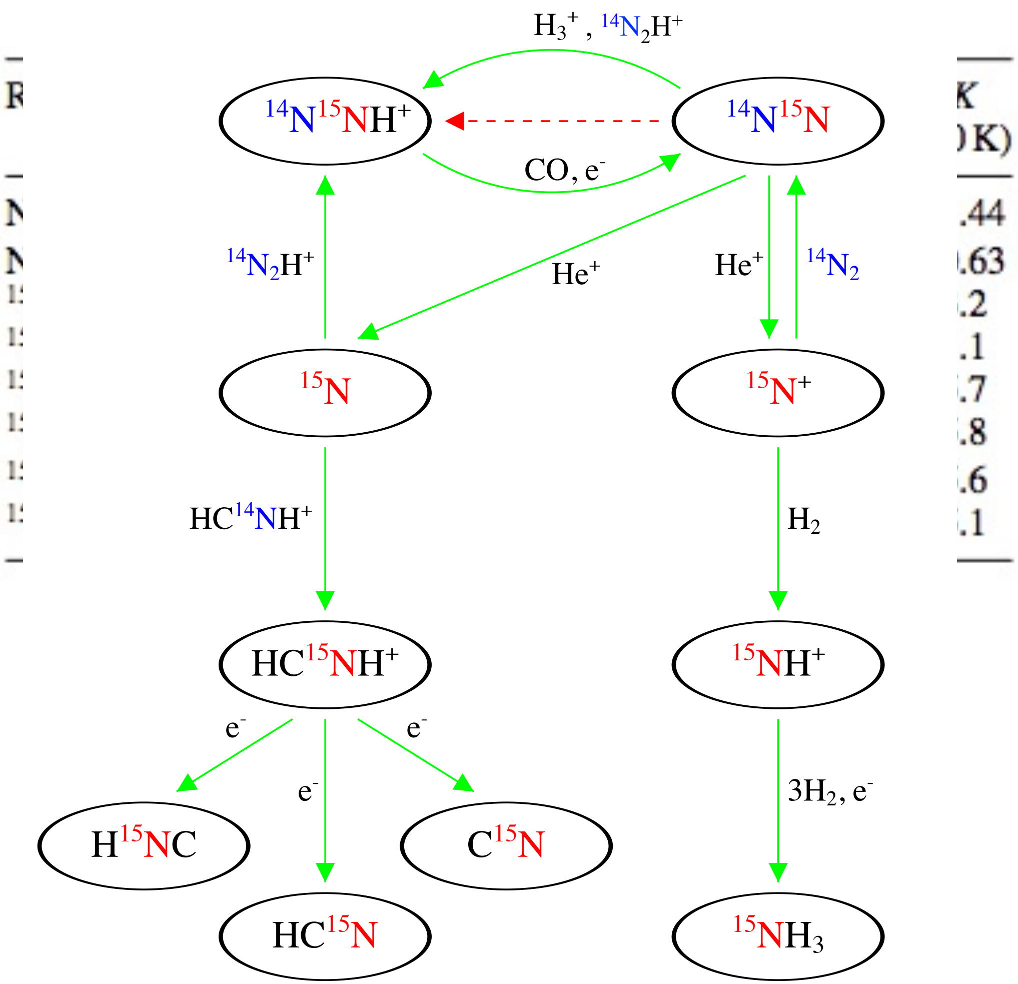
# Nitrogen fractionation models

| Reaction | $f(B,m)$ (10 K) | $\Delta E_0/k$ (K) | $K$ (10 K) |
|---|---|---|---|
| $N^{15}N + HN_2^+ \rightleftharpoons N_2 + H^{15}NN^+$ | 0.494 | 10.7 | 1.44 |
| $N^{15}N + HN_2^+ \rightleftharpoons N_2 + HN^{15}N^+$ | 0.499 | 2.25 | 0.63 |
| $^{15}N^+ + N_2 \rightleftharpoons N^+ + N^{15}N$ | 1.959 | 28.3 | 33.2 |
| $^{15}N^+ + NO \rightleftharpoons N^+ + {}^{15}NO$ | 0.979 | 24.3 | 11.1 |
| $^{15}N + CNC^+ \rightleftharpoons N + C^{15}NC^+$ | 0.938 | 36.4 | 35.7 |
| $^{15}N + HN_2^+ \rightleftharpoons N + H^{15}NN^+$ | 0.968 | 36.1 | 35.8 |
| $^{15}N + HN_2^+ \rightleftharpoons N + HN^{15}N^+$ | 0.977 | 27.7 | 15.6 |
| $^{15}N + HCNH^+ \rightleftharpoons N + HC^{15}NH^+$ | 0.968 | 35.9 | 35.1 |

**Terzieva & Herbst (2000)**

- Fractionation effect too minor to be detectable

# Nitrogen fractionation models – depletion cores




**Rodgers & Charnley (2008a,b)**

- High density (1e6 $cm^{-3}$), CO depletion, and low temperature (10 K) → $^{14}N/^{15}N \geq 50$
- Main $^{15}N$ pool: initially molecular (and atomic?)

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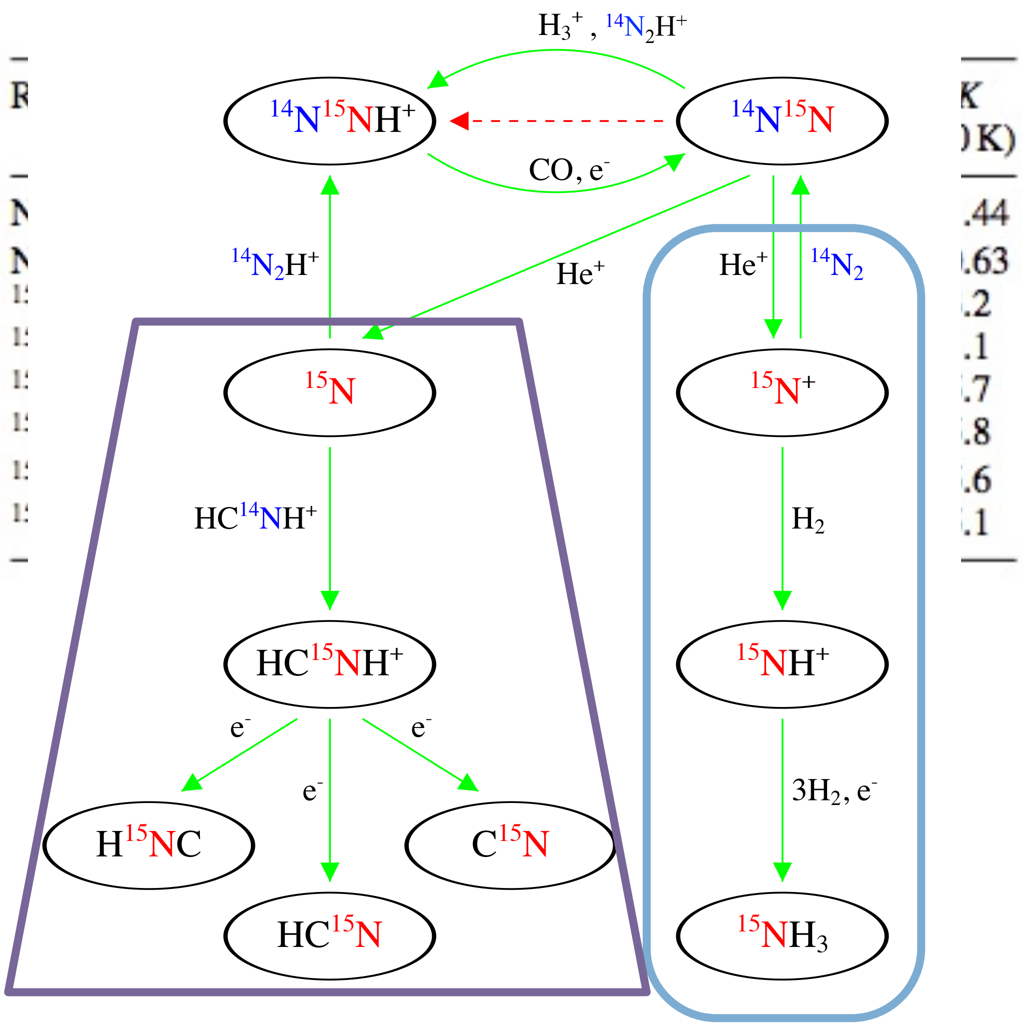


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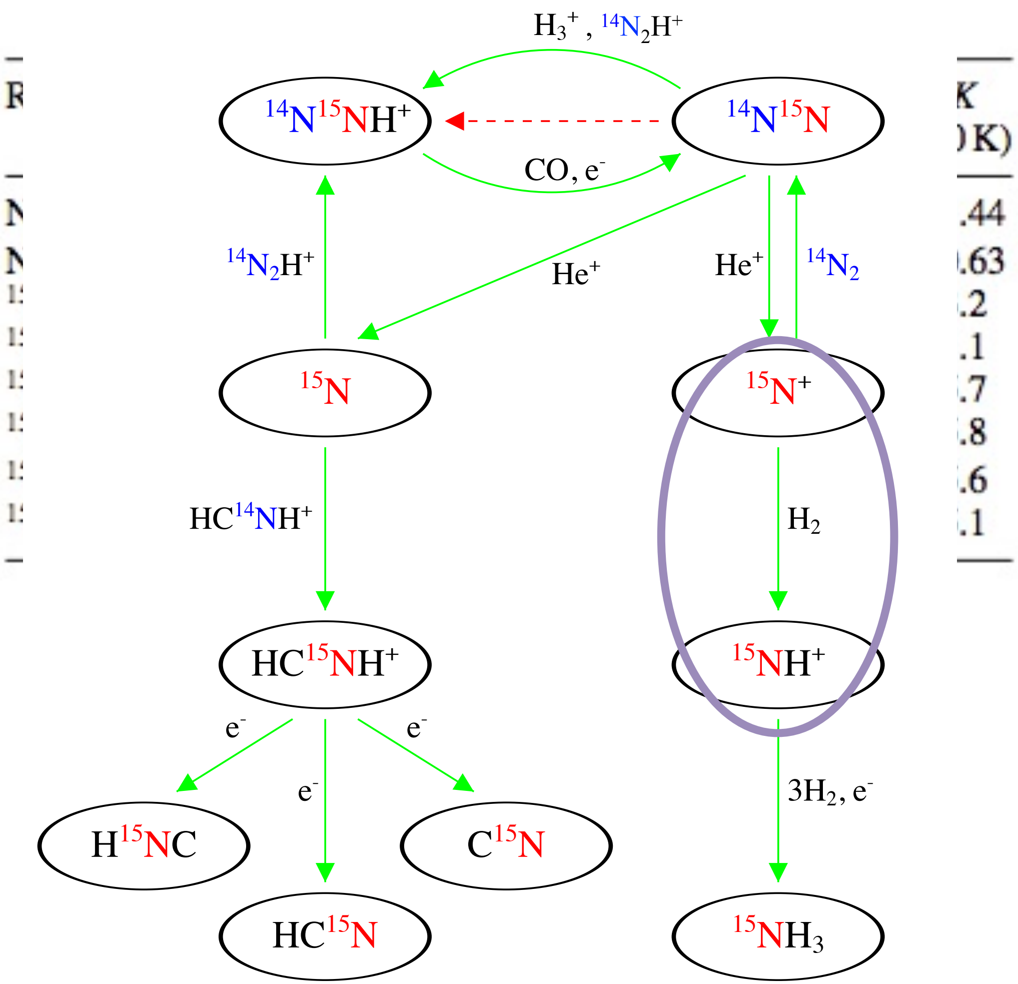
- High density (1e6 cm$^{-3}$), CO depletion, and low temperature (10 K)
  → $^{14}N/^{15}N \geq 50$
- Main $^{15}$N pool: initially molecular (and atomic?)
- Separate $^{15}$N routes for Nitriles and Amines

→ different fract. timescales

# Nitrogen fractionation models – depletion cores




**Wirström et al. (2012)**

$$N^+ + o\text{-}H_2 \longrightarrow NH^+ + H$$

- Effective at low T, but rate overestimated (T dep.) (Le Bourlot, 1991; Dislaire et al., 2012)

→ low $o\text{-}H_2$ suppress $^{15}N$ fractionation in $NH_3$

- No effect on nitriles

→ More pronounced difference btw Nitriles and Amines

(also Hily-Blant et al., 2013)

# N fractionation in depletion cores (before 2015)

The Astrophysical Journal Letters, 757:L11 (5pp), 2012 September 20 Wirström et al.

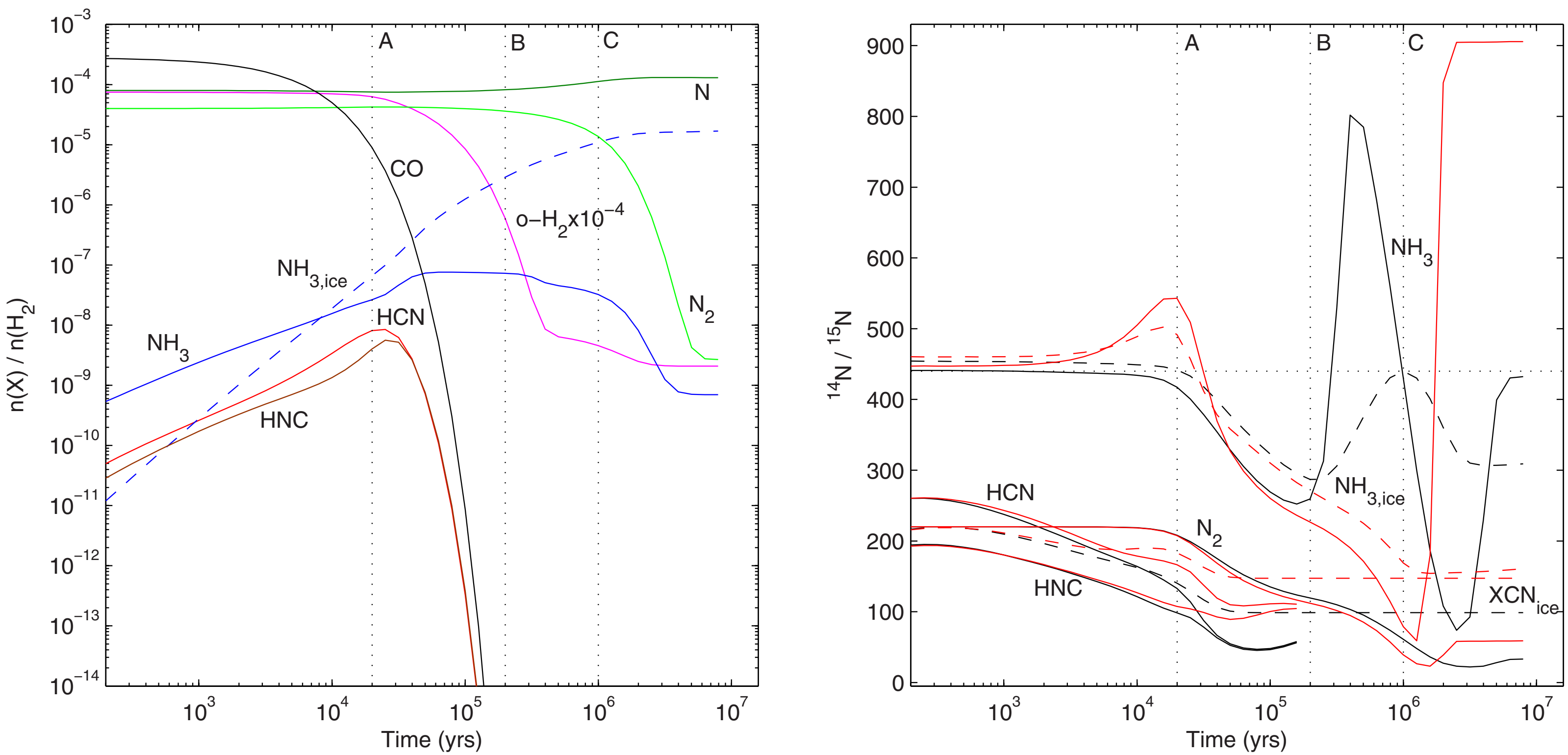



**Figure 2.** Left panel: time evolution of the nitrogen chemistry in dense cores, compared to CO and $o$-$H_2$. Crucial times for the $^{15}$N fractionation in nitrogen hydrides

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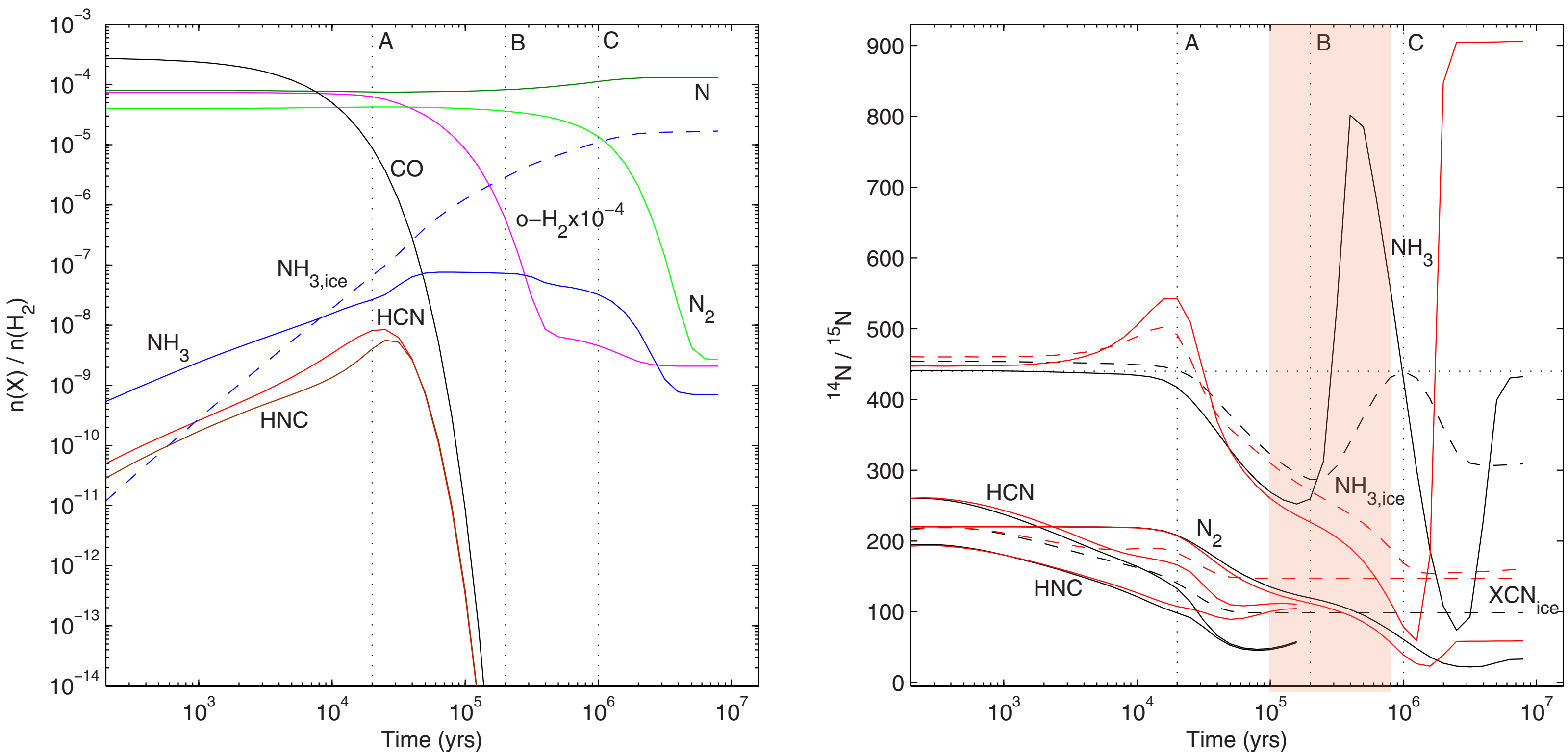
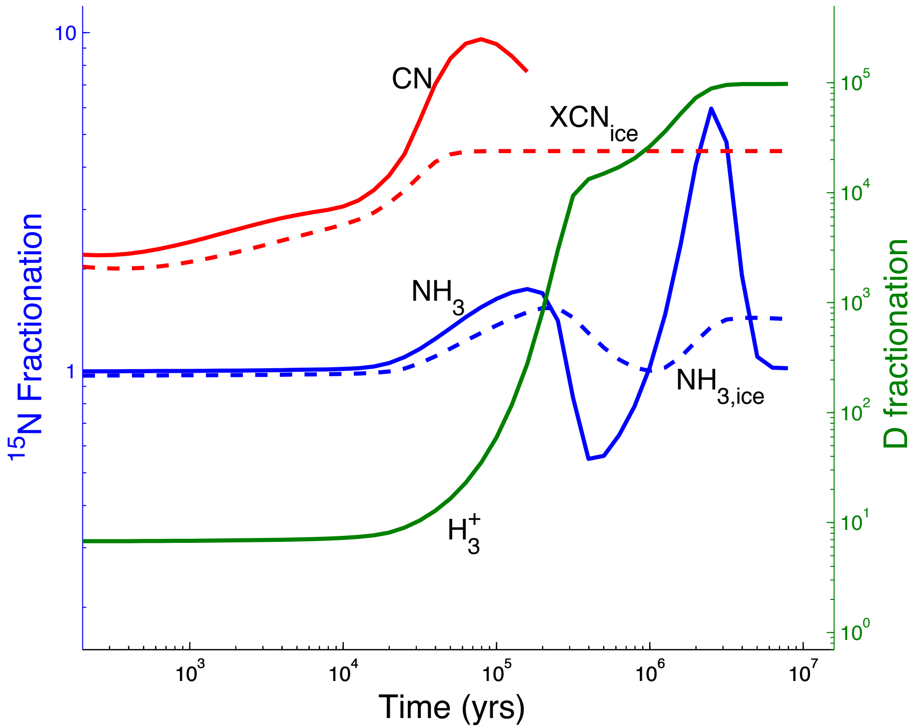



**Figure 2.** Left panel: time evolution of the nitrogen chemistry in dense cores, compared to CO and $o$-$H_2$. Crucial times for the $^{15}N$ fractionation in nitrogen hydrides

Typical core lifetimes (e.g. Crapsi et al 2005)

# N fractionation in depletion cores (before 2015) – including D fractionation into $H_2D^+$

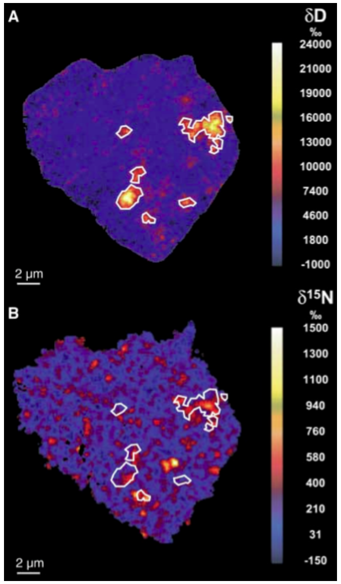



$^{15}$N frac rel. to $^{15}N/^{14}N = 1/440$

Wirström et al. (2012)

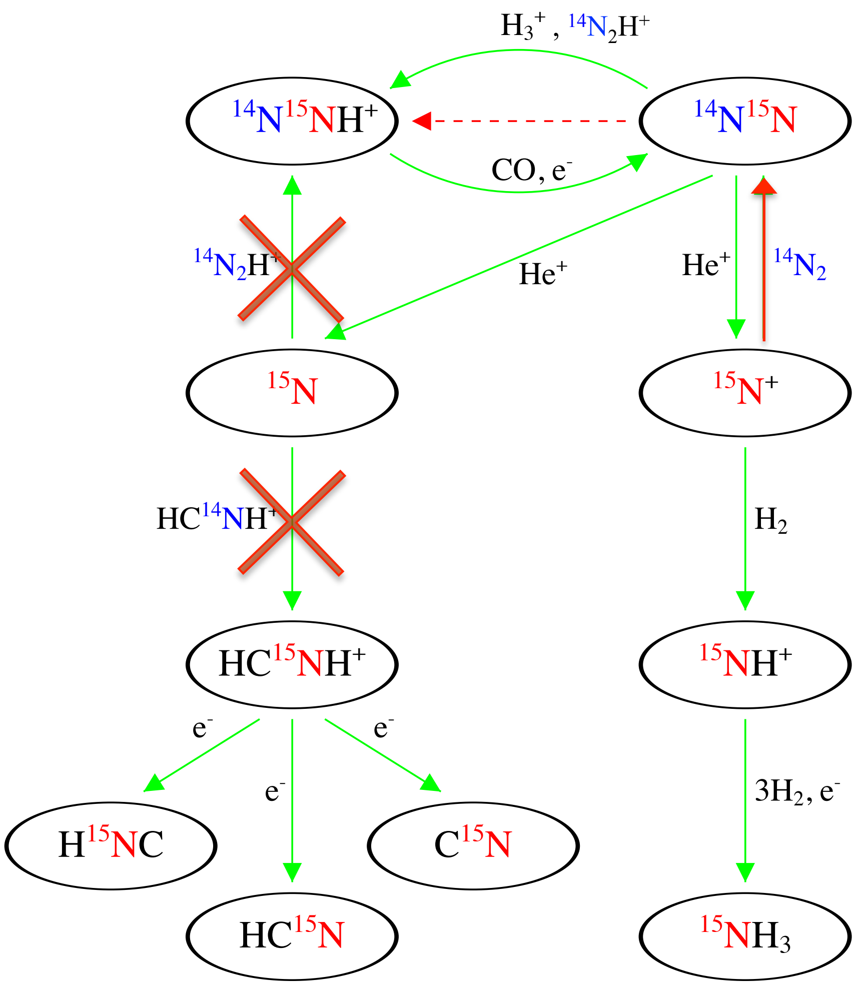
Nitriles:
- Highest $^{15}$N enrichments
- D enrichment

Amines:
- $^{15}$N and D enrichment, or…
- Very D enriched and $^{15}$N depleted,




Busemann et al (2006)

# Interstellar nitrogen fractionation – models




**Roueff et al. (2015)**

- Updated reaction rates based on ZPE's & barrier evaluation

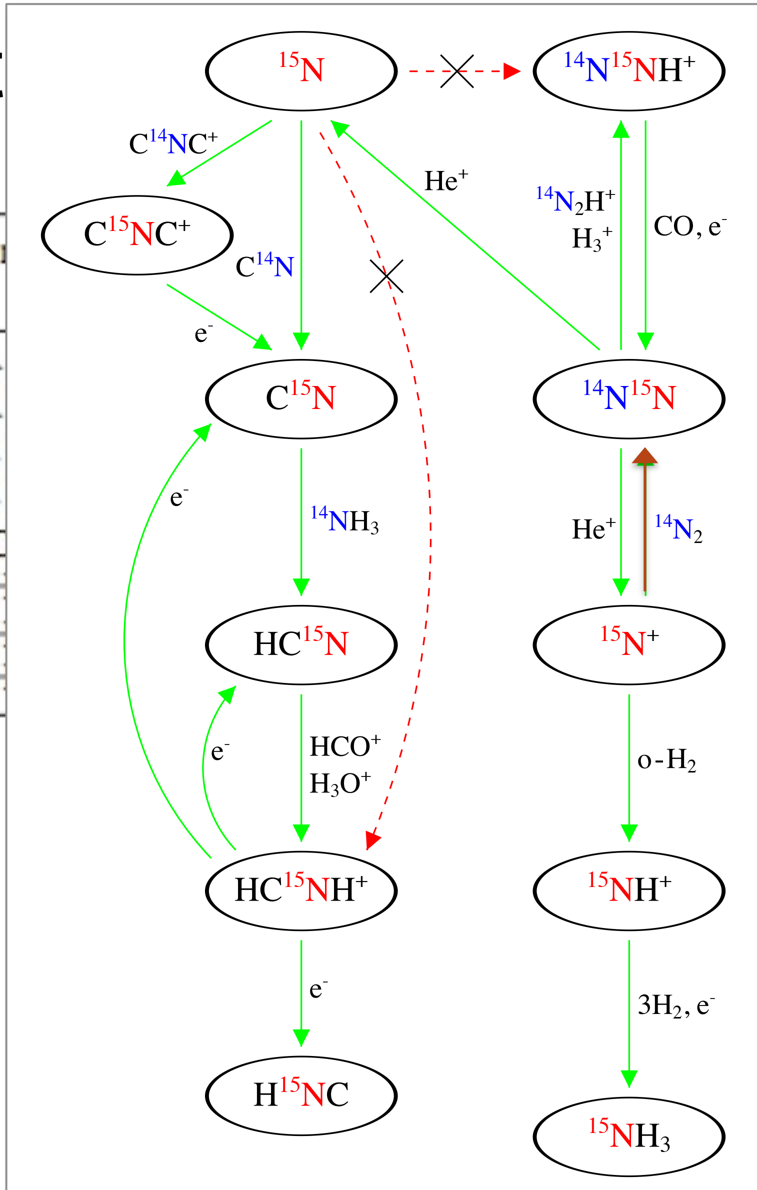
→ significant barriers in reactions suppress $^{15}N$ fractionation from atomic $^{15}N$

→ $^{15}N^+$ is more efficiently circulated back into $N^{15}N$

- Demonstrates coupling btw N, C, and H fractionation

Loison talk

# Nit… models – depletion cores




| Reaction… | $K$ (10 K) |
|---|---|
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| $^{15}N^+$ + … | 33.2 |
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| $^{15}N$ + H… | 15.6 |
| $^{15}N$ + H… | 35.1 |

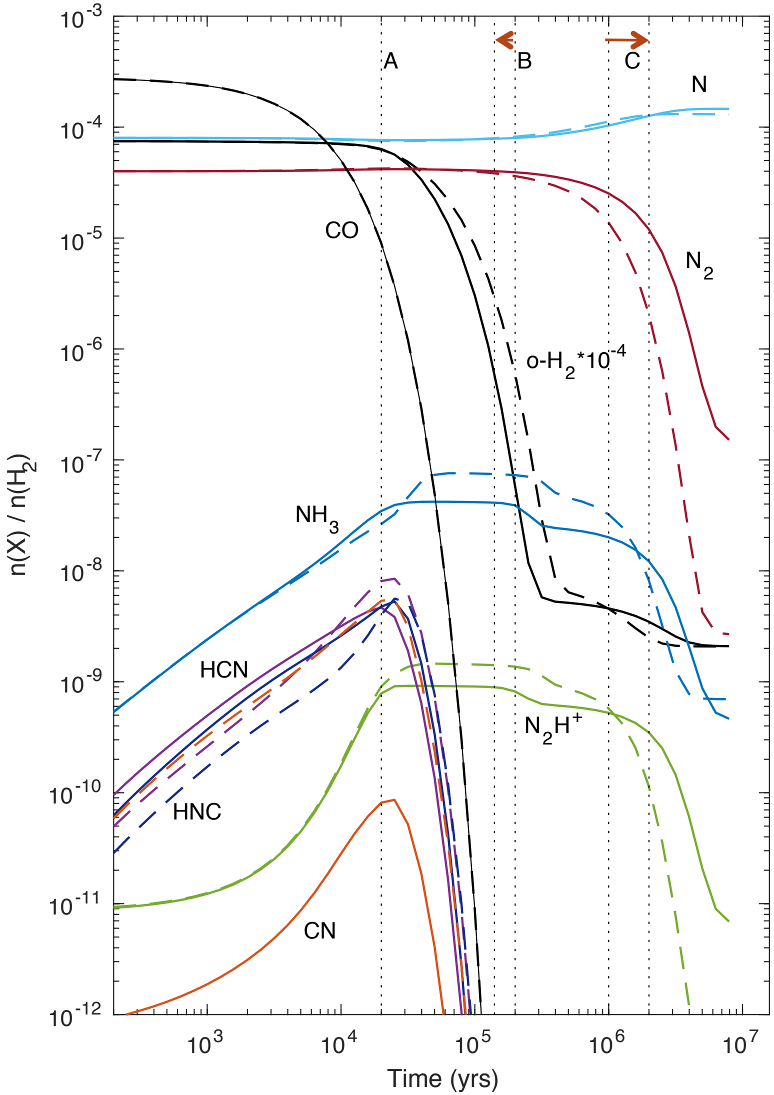
**Wirström & Charnley (2017, accepted in MNRAS)**

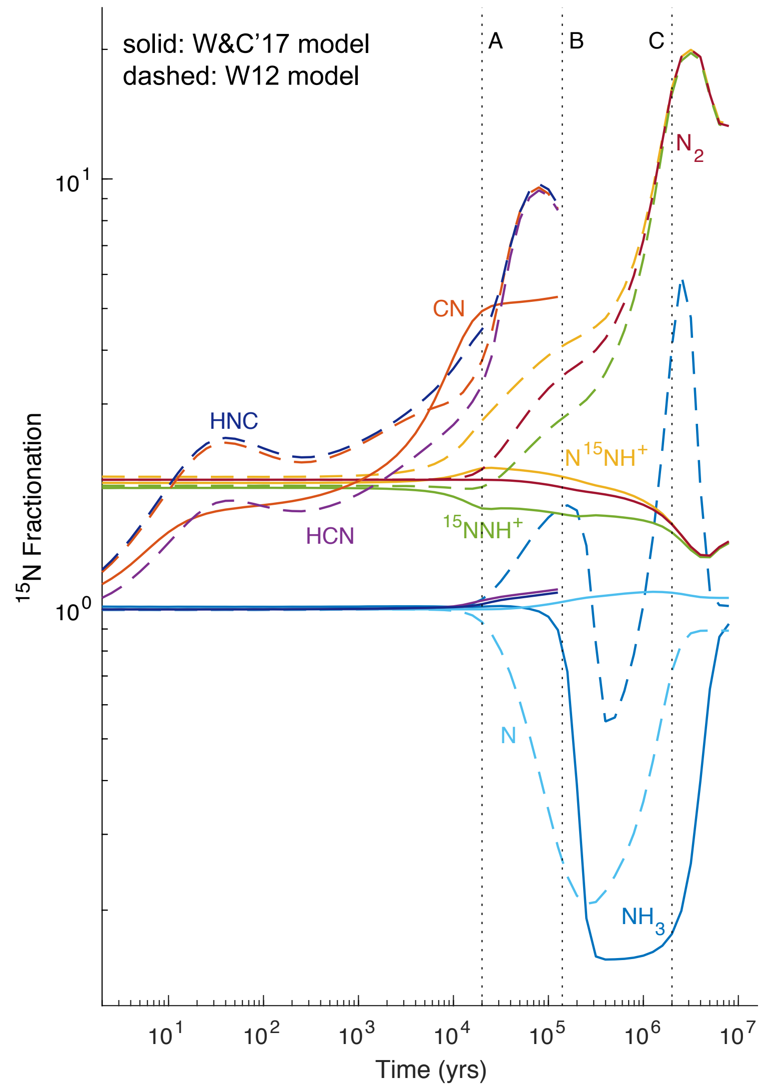
Updated Wirström'12:

- Roueff'15 fractionation rates
- Updated N-chemistry:
  - Wakelam'13, '15
  - Including $C_2N$ species
  - Updated DR rates ($NH^+$, $N_2H^+$) based on exp. (Novotny+14,Molek+07, Vigren+12)
  - Grozdanov+'16 isotope-specific rates for

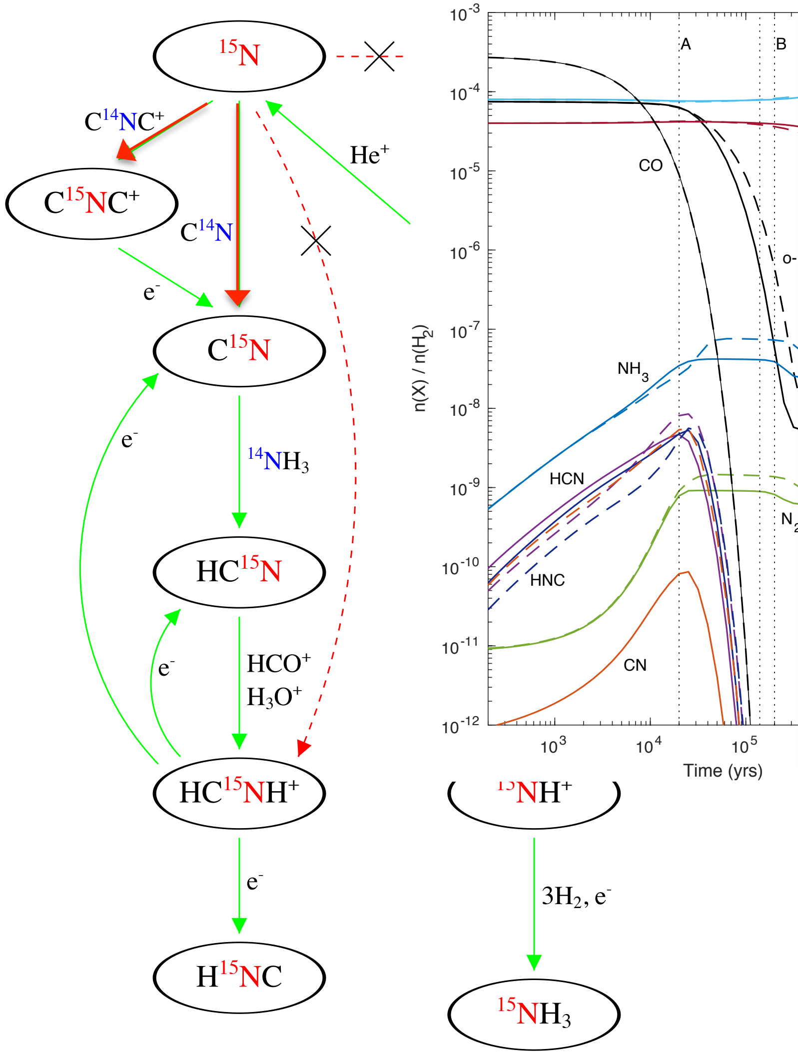
$$N^+ + o/p\text{-}H_2 \longrightarrow NH^+ + H$$

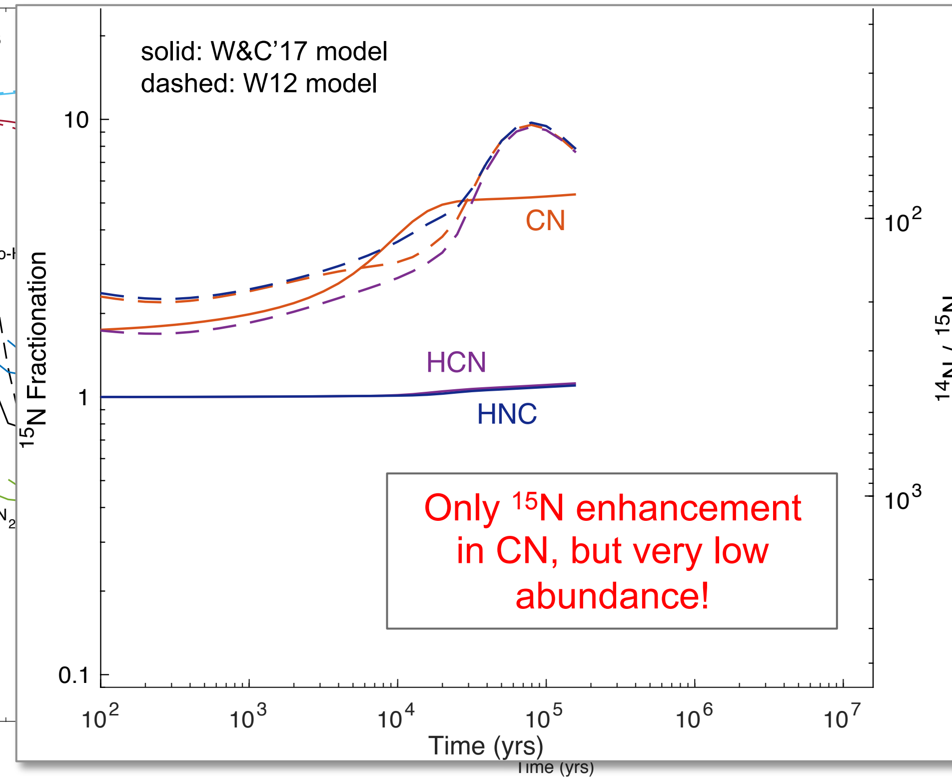
# Wirström & Charnley'17 model – Timescales



# Wirström & Charnley’17 model – Nitriles

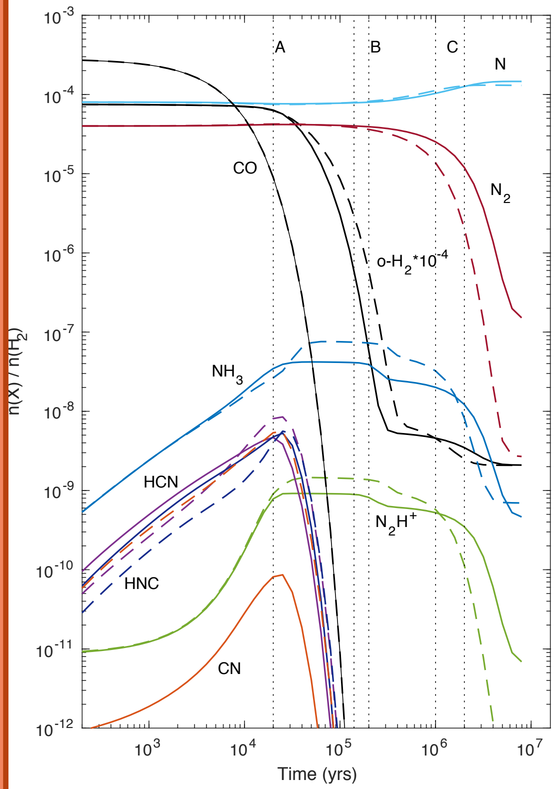


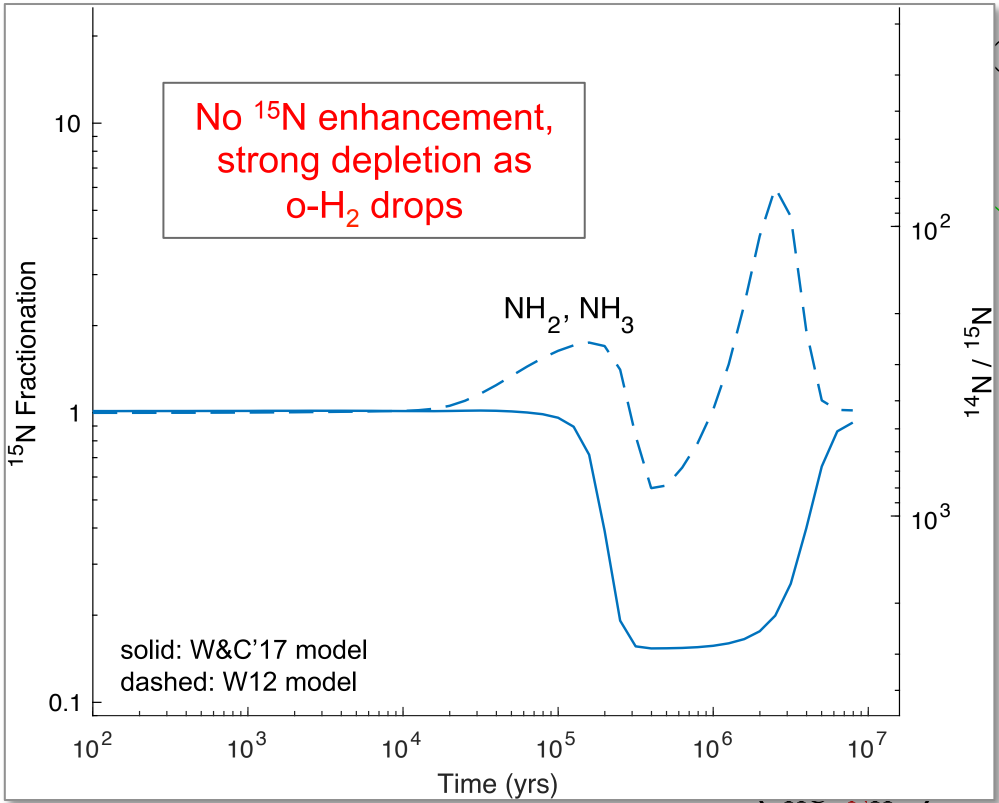



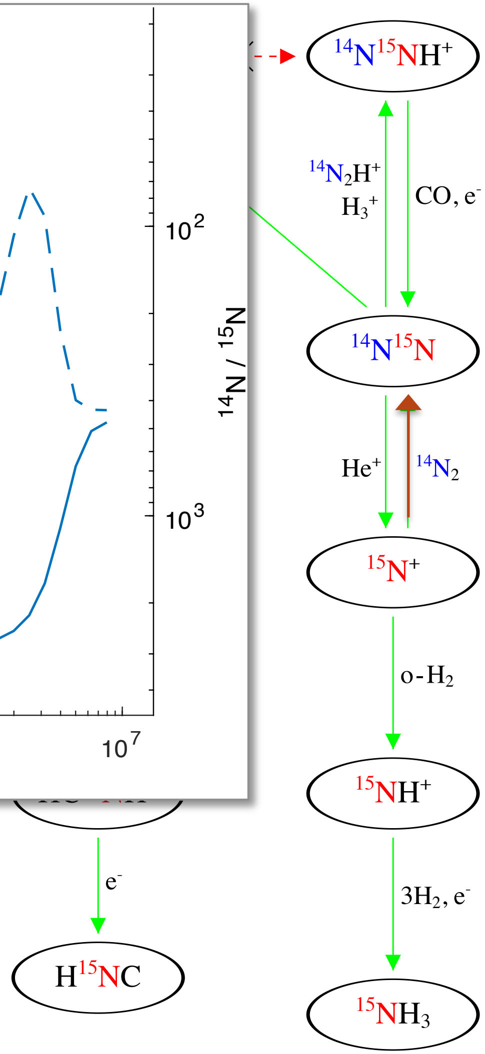

$$N + CN \longrightarrow N_2 + C$$

Lab measurements by Daranlot et al. (2012)

# Wirström & Charnley'17 model – Amines



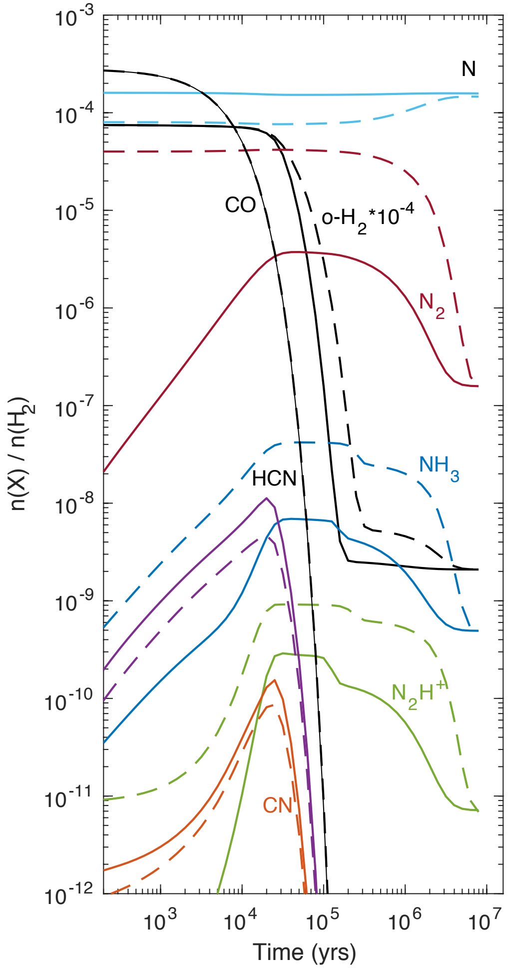



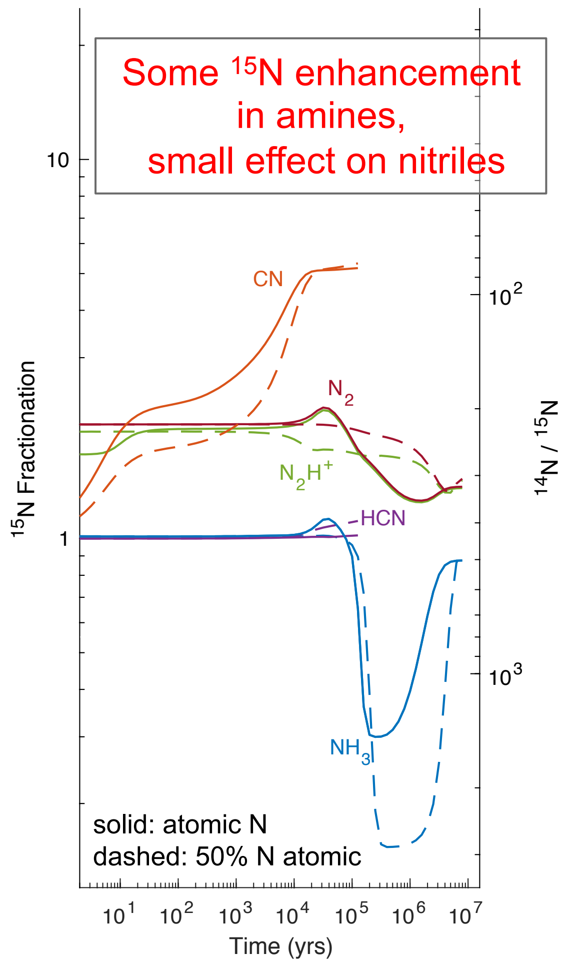



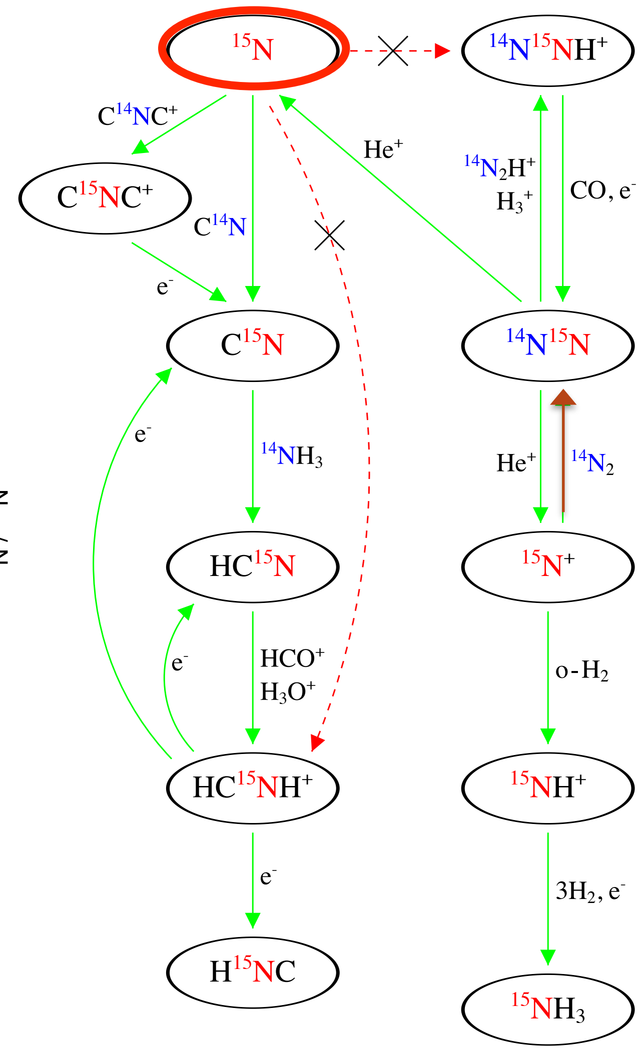

$$^{15}N^+ + N_2 \rightleftharpoons N^+ + N^{15}N$$

Higher K(10 K) from Roueff et al. (2015)

# Wirström & Charnley'17 model – atomic N reservoir?



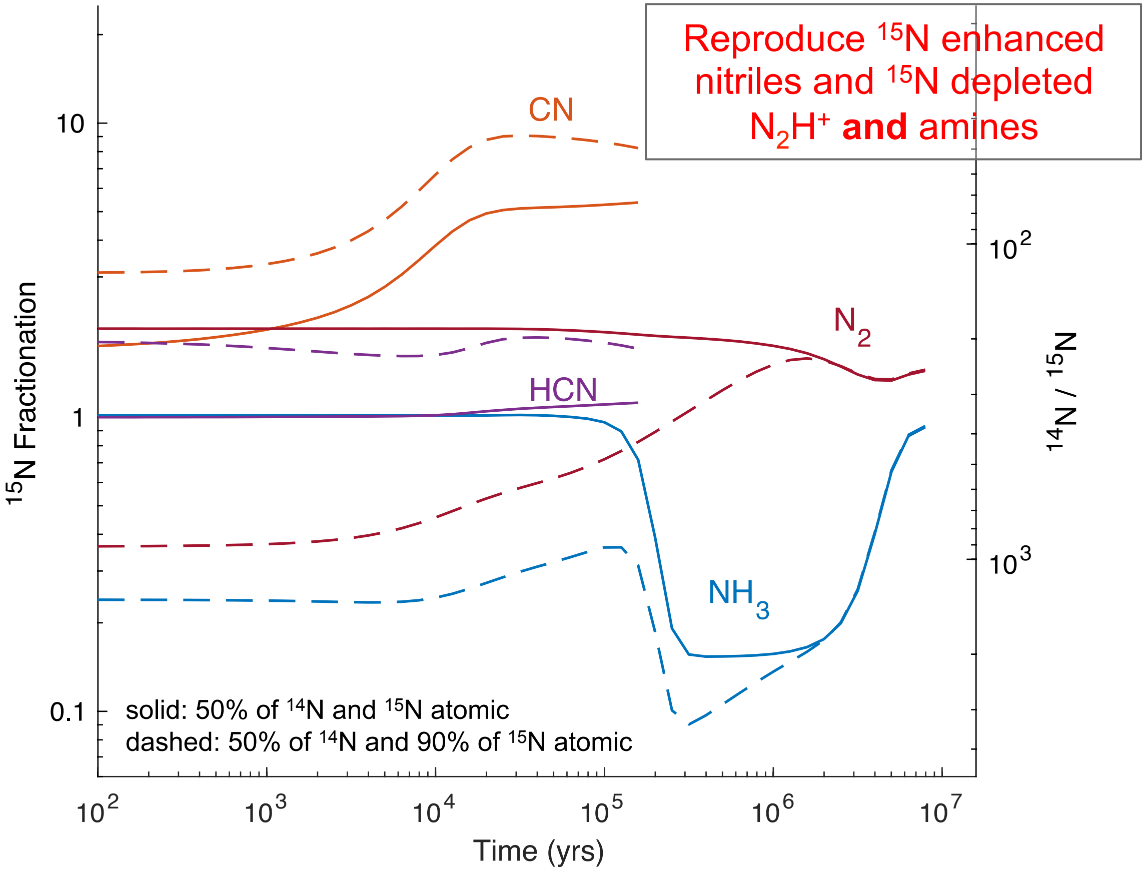



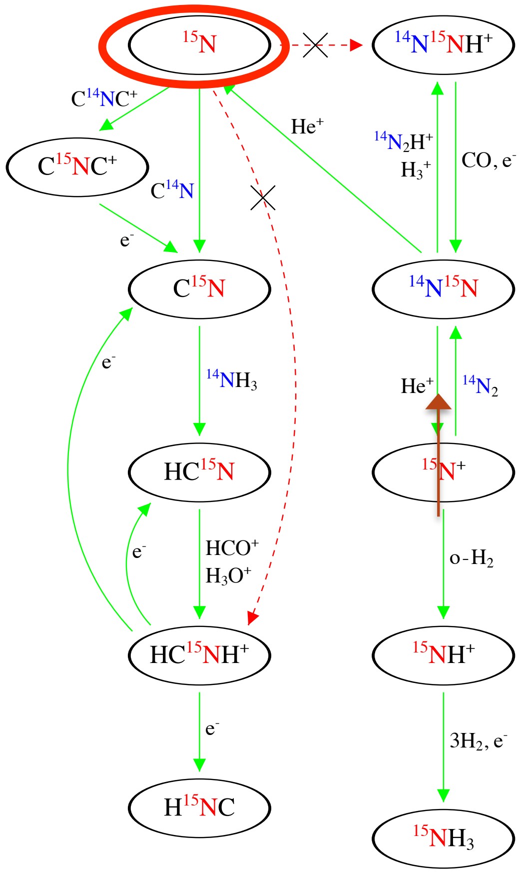



# Wirström & Charnley'17 model – atomic $^{15}N$?

E.g. suggested for PSN by Hily-Blant et al (2017)

Reproduce $^{15}N$ enhanced nitriles and $^{15}N$ depleted $N_2H^+$ **and** amines




$N_2H^+$ fractionation follows closely $N_2$

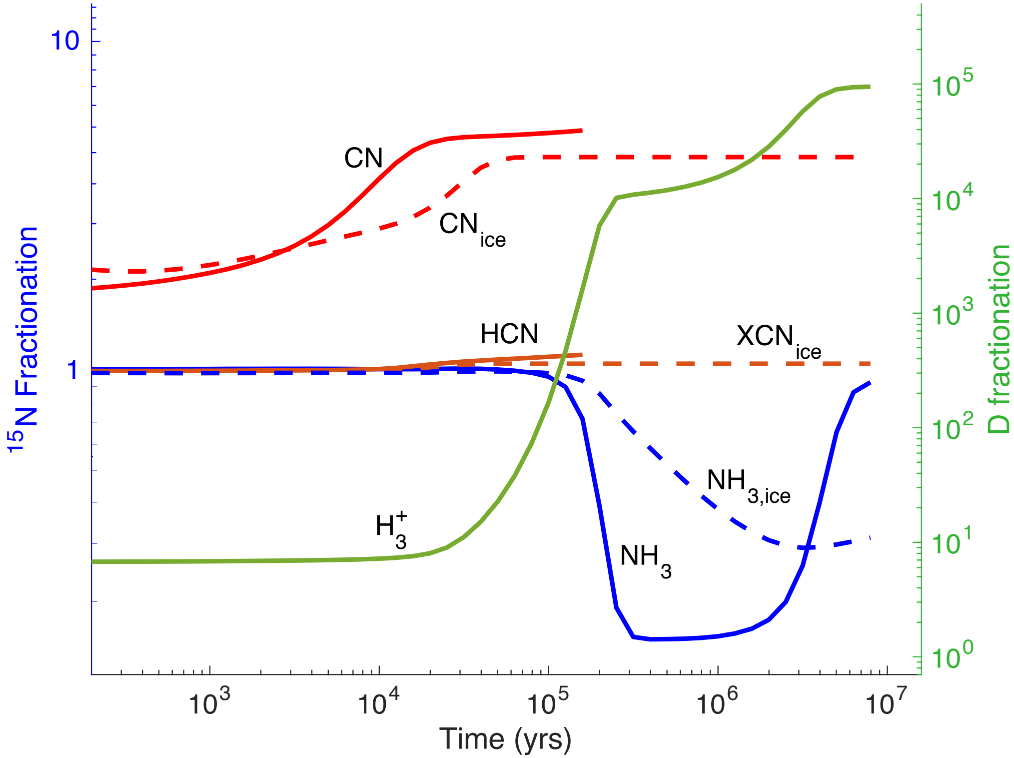
Photodissociation fractionation -> $^{15}N/^{14}N > N^{15}N/N_2$

# Wirström & Charnley'17 model – $^{15}$N & D in functional groups of ices

Chondrite material
(van Kooten+17)

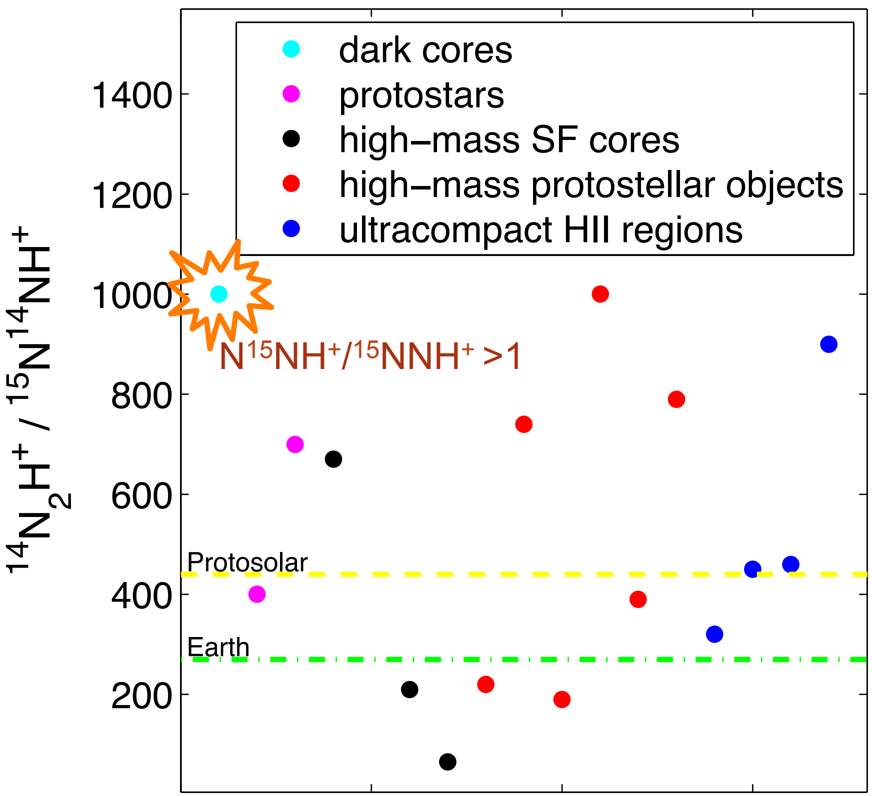
A-type:
$^{15}$N rich & D rich ?!
= NITRILES

H-type:
$^{15}$N poorer & D rich !
= AMINES



# The $N_2H^+$ problem

## Observations

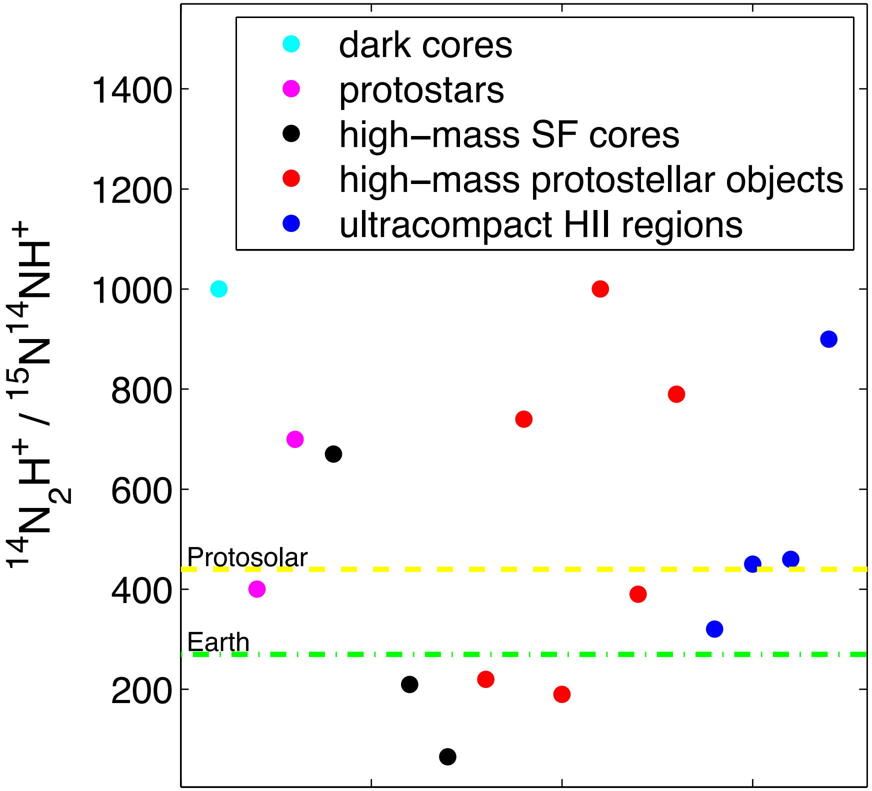



Bizzocchi L, et al. (2013). Daniel et al. (2013). Cordiner et al. in prep. Massive SF sources: Fontani et al. (2015).

## Models

- Wirström et al (2012): $^{14}N/^{15}N$ in $N_2H^+$=100-300, $N^{15}NH^+/^{15}NNH^+$>1
- Roueff et al (2015): Both $N_2H^+$ $^{14}N/^{15}N$ ratios ~ elemental

# The $N_2H^+$ problem – Temp effect in HMSF?

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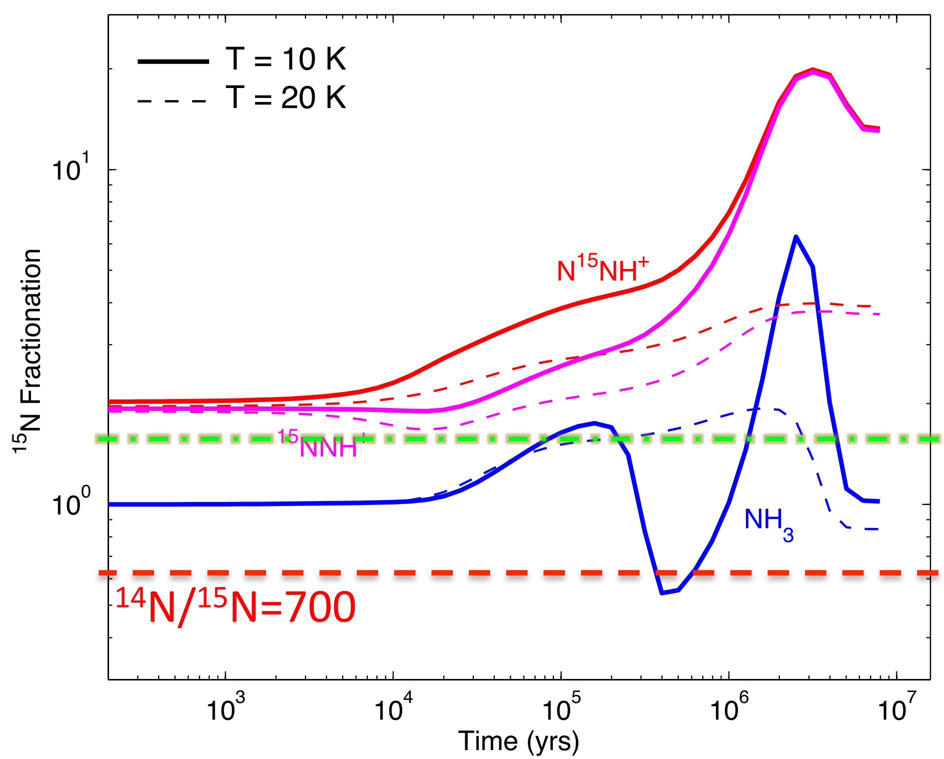
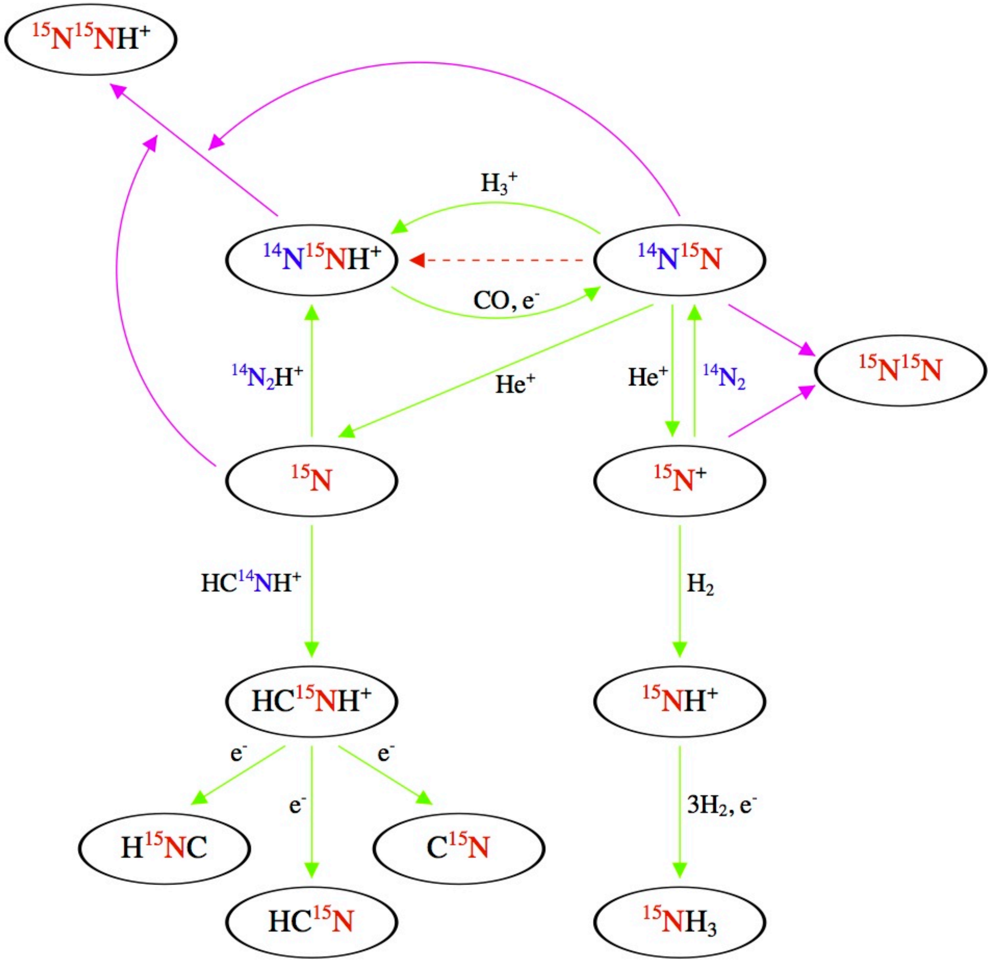
2012 model at 20 K



# The $N_2H^+$ problem – possible $^{15}N_2$ fractionation




- Wirström'12 model, including direct fractionation to doubly exchanged $N_2$ species
- Optimistic reaction rates estimated from ΔZPE's

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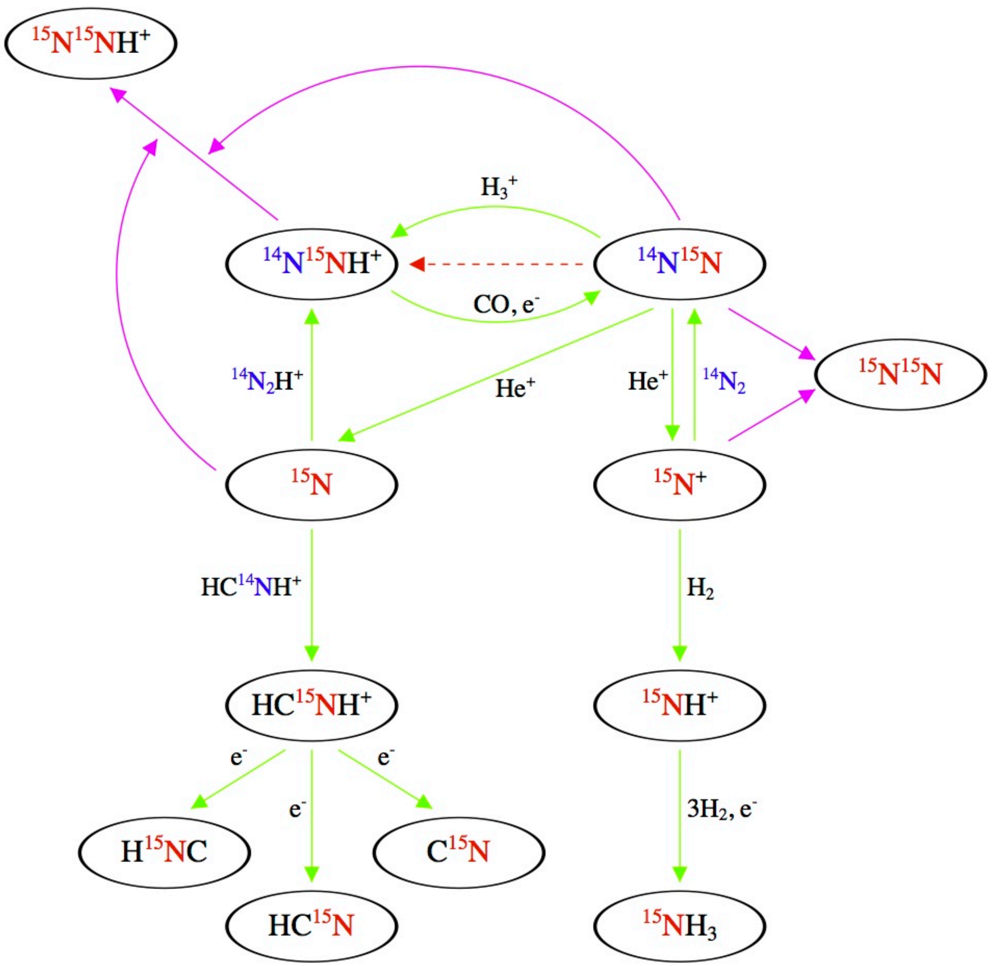


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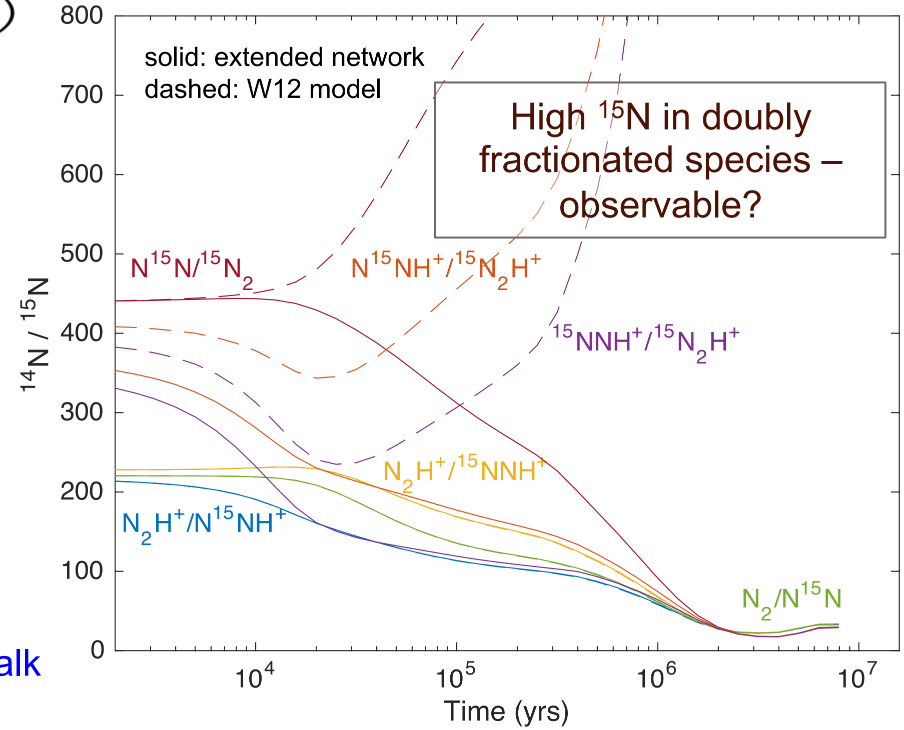


Dore et al. (2017) + Bizzocchi talk

# Summary and outstanding issues

Disequilibrium ion-molecule chemistry under cold, dense cloud conditions, including full $H_2$ OPR treatment and freeze-out, predicts:

- Suppressed HCN and HNC fractionation, only CN may carry $^{15}N$ enhancements – Barriers of relevant isotopic exchange reactions need to be re-evaluated for range of interaction geometries?
- High $^{14}N/^{15}N$ ratios in amines, but ices still D enhanced – in rough agreement with non-correlations btw hotspots in primitive materials
- An increased atomic fraction of $^{15}N$ produce nitriles with lower and $N_2H^+$ with higher $^{14}N/^{15}N$ ratios, ie closer to what is observed in ISM – How relevant?

In addition:

- All current models fail to reproduce low observed $^{15}N$ in $N_2H^+$ in dark clouds and high $^{15}NH_3$ in comets – Need to be addressed
- Alternative fractionation bimolecular reactions? Neutral processes?
- Spectroscopy available for doubly $^{15}N$ substituted $N_2H^+$ – Can observations provide further constraints?