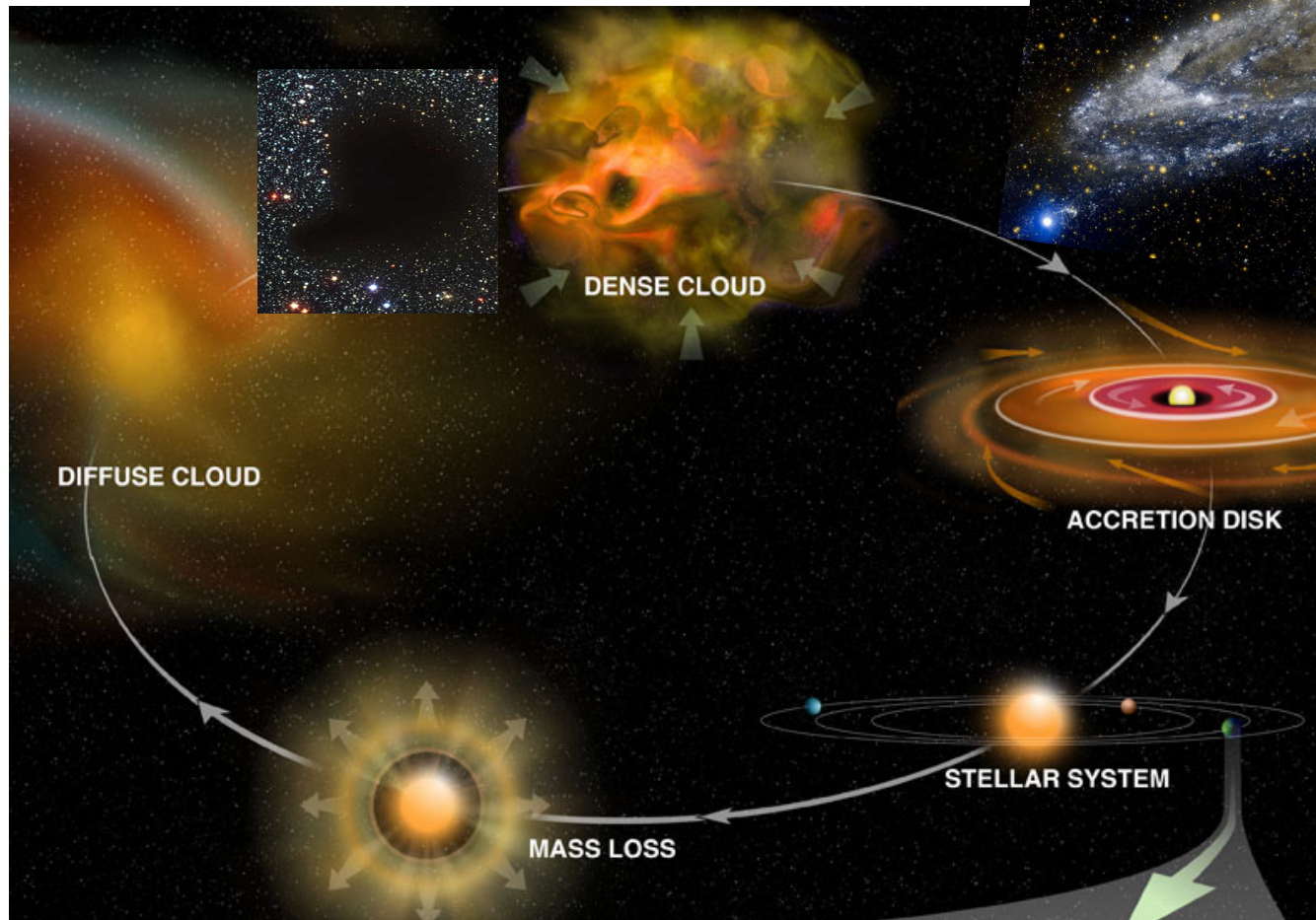


Fractionation in dark pre-stellar clouds

Eva Wirström
Department of Earth and Space Sciences
Onsala Space Observatory
Chalmers, Sweden

Fractionation of isotopes in space, Florence, October 2016

Our isotope tools



Observed line ratios are combinations of:

- a) Elemental abundance ratios set by BB and local history of nucleosynthesis (star formation)
- b) Fractionation processes
- c) Excitation and radiative transfer effects (data interpretation)

Elemental abundances

	Solar System	local ISM
D / H	2.00×10^{-5} ⁽¹⁾	1.6×10^{-5} ⁽⁴⁾
$^{12}\text{C} / ^{13}\text{C}$	89.4 ⁽¹⁾	69 ± 6 ⁽⁴⁾
$^{14}\text{N} / ^{15}\text{N}$	441 ± 6 ⁽³⁾	388 ± 32 ⁽⁴⁾
$^{16}\text{O} / ^{18}\text{O}$	499 ⁽¹⁾	557 ± 30 ⁽⁴⁾
$^{18}\text{O} / ^{17}\text{O}$	5.3 ⁽¹⁾	3.6 ± 0.2 ⁽⁴⁾
$^{32}\text{S} / ^{34}\text{S}$	22.5 ⁽²⁾	24 ± 5 ⁽⁵⁾
$^{34}\text{S} / ^{33}\text{S}$	5.6 ⁽²⁾	6.3 ± 1.0 ⁽⁵⁾
$^{28}\text{Si} / ^{29}\text{Si}$	19.7 ⁽²⁾	
$^{29}\text{Si} / ^{30}\text{Si}$	1.5 ⁽²⁾	1.5 ⁽⁴⁾

- (1) Asplund et al. 2009, ARA&A, 47, 481
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- (3) Marty et al. 2011, Science 332, 1533
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Elemental abundances

	Solar System	local ISM
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- D formed only in Big Bang Nucleosynthesis
- D burned to ^4He in stars and brown dwarfs
- D/H decrease with stellar processing

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- ^{12}C formed from He in triple- α process (primary)
- ^{13}C formed in CNO cycle ($>1M_{\text{Sun}}$ stars)
- $^{12}\text{C}/^{13}\text{C}$ decrease with secondary stellar processing

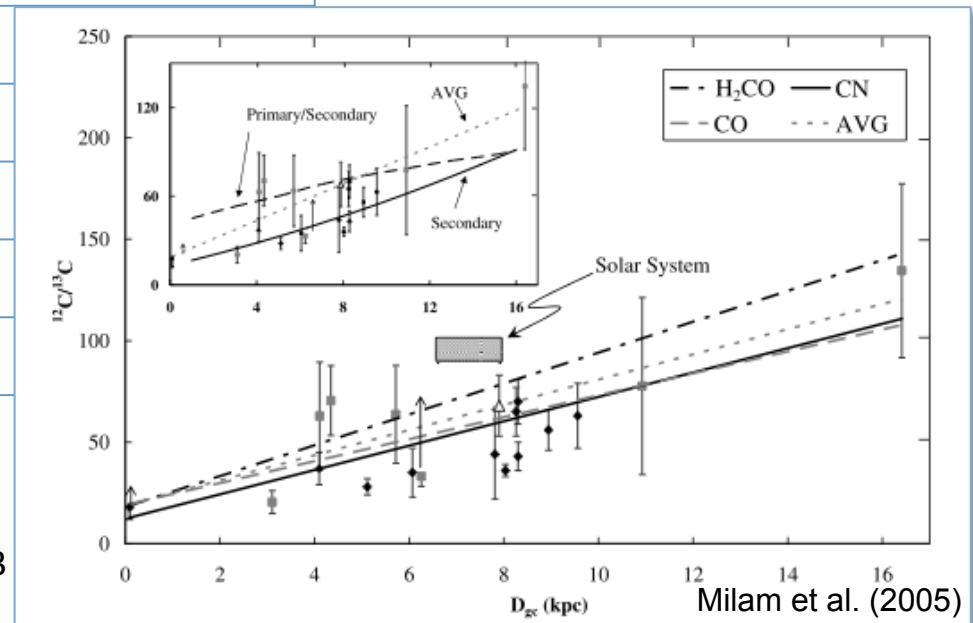
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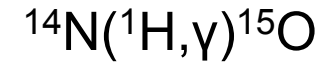


- ^{14}N builds up in the cold CNO cycle
- ^{15}N build up from ^{15}O in the hot CNO cycle
- $^{14}\text{N}/^{15}\text{N}$ should decrease with massive stellar processing

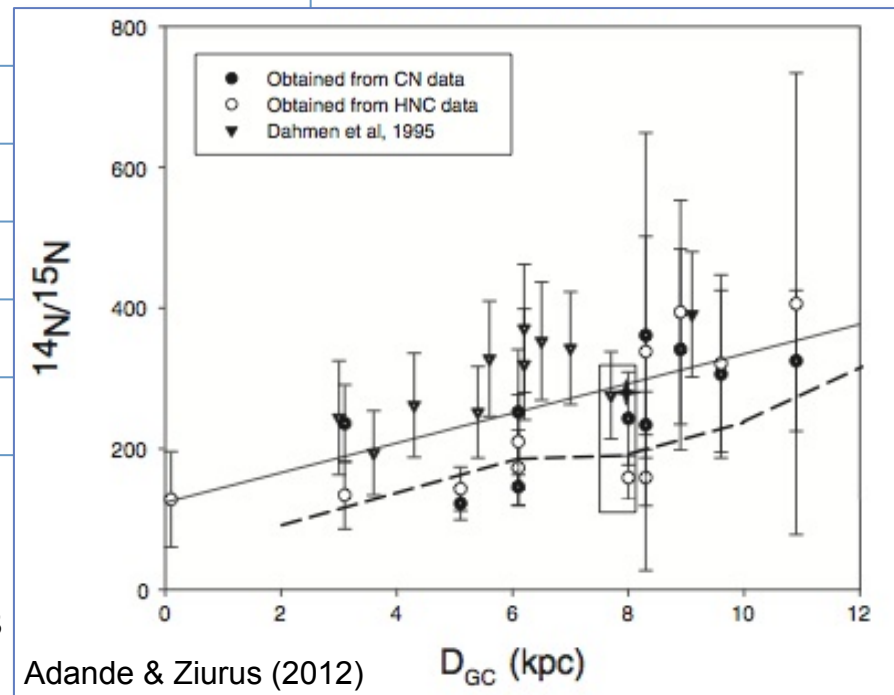
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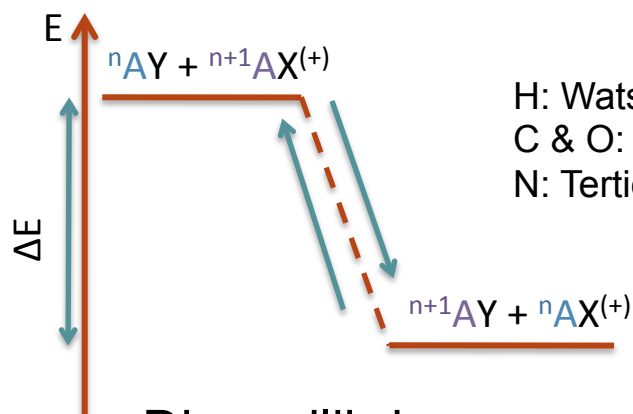
Ne and O burning (SNe)
e.g. [Henkel](#), [Podio](#)

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Observed line ratios are combinations of:

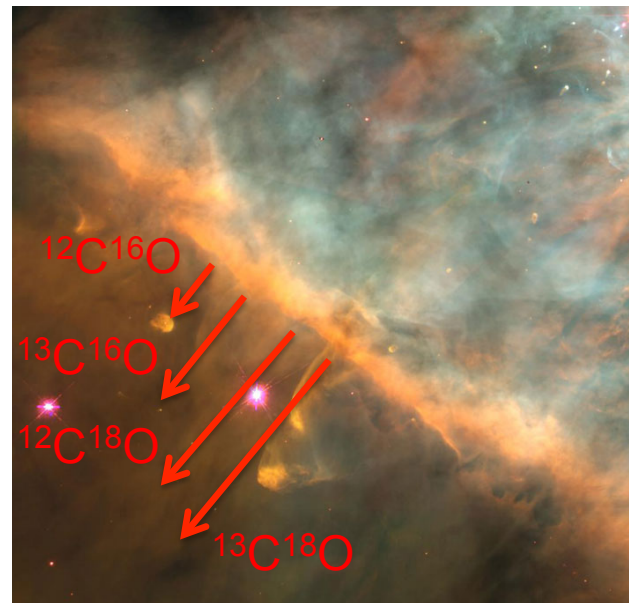
- a) Elemental abundance ratios set by BB and local history of nucleosynthesis (star formation)
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Isotope fractionation processes



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

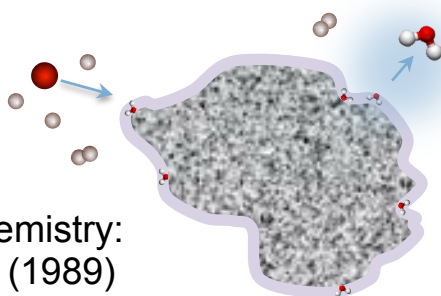
Disequilibrium gas-phase chemistry



Self-shielding against photodissociation

H₂: Watson (1973)
CO: van Dishoeck & Black (1988)
N₂: Heays et al. (2014)

Gas-grain interaction



Lamberts,
Taquet

Surface/ice chemistry:
Brown & Millar (1989)

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

Conditions in dark pre-stellar cores



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

Cold: $T \approx 5 - 15 \text{ K}$

Dense: $n(\text{H}_2) \sim 1\text{e}5\text{-}7 \text{ cm}^{-3}$

Dark: $A_V > 10 \text{ mag}$

- CO etc. frozen on dust
- N_2 (N_2H^+) still in gas
- High atomic D/H

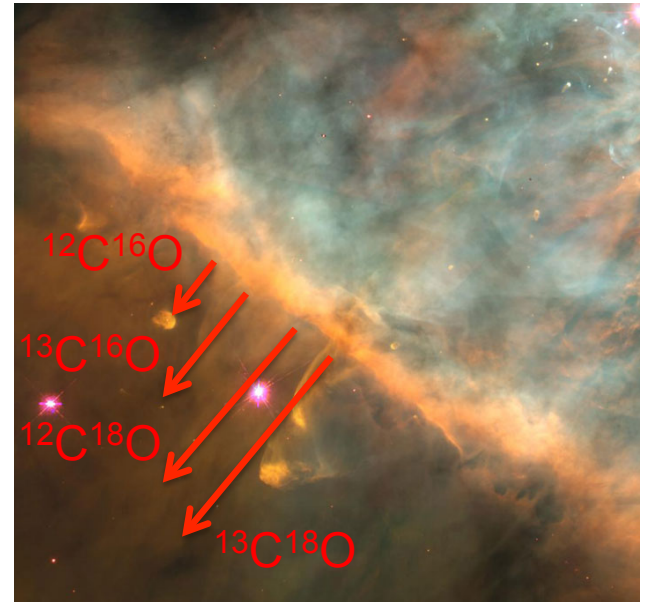
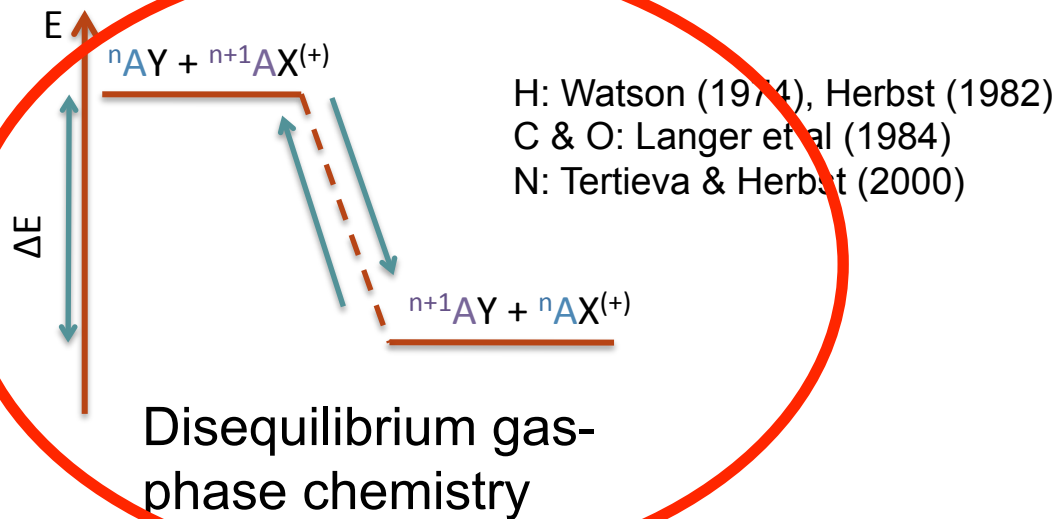


Disequilibrium chemistry

Gas-grain interaction

~~Energetic photon interactions~~

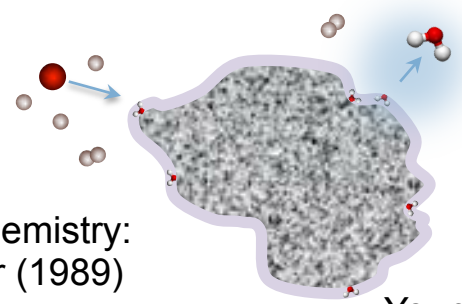
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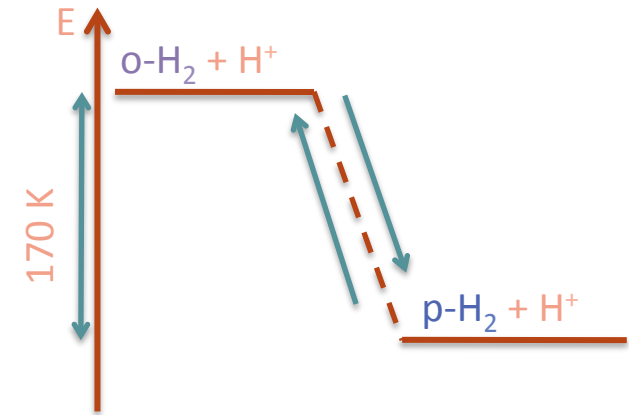
Mass dependence:
Young & Schauble (2011);
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Nuclear spin type dependence

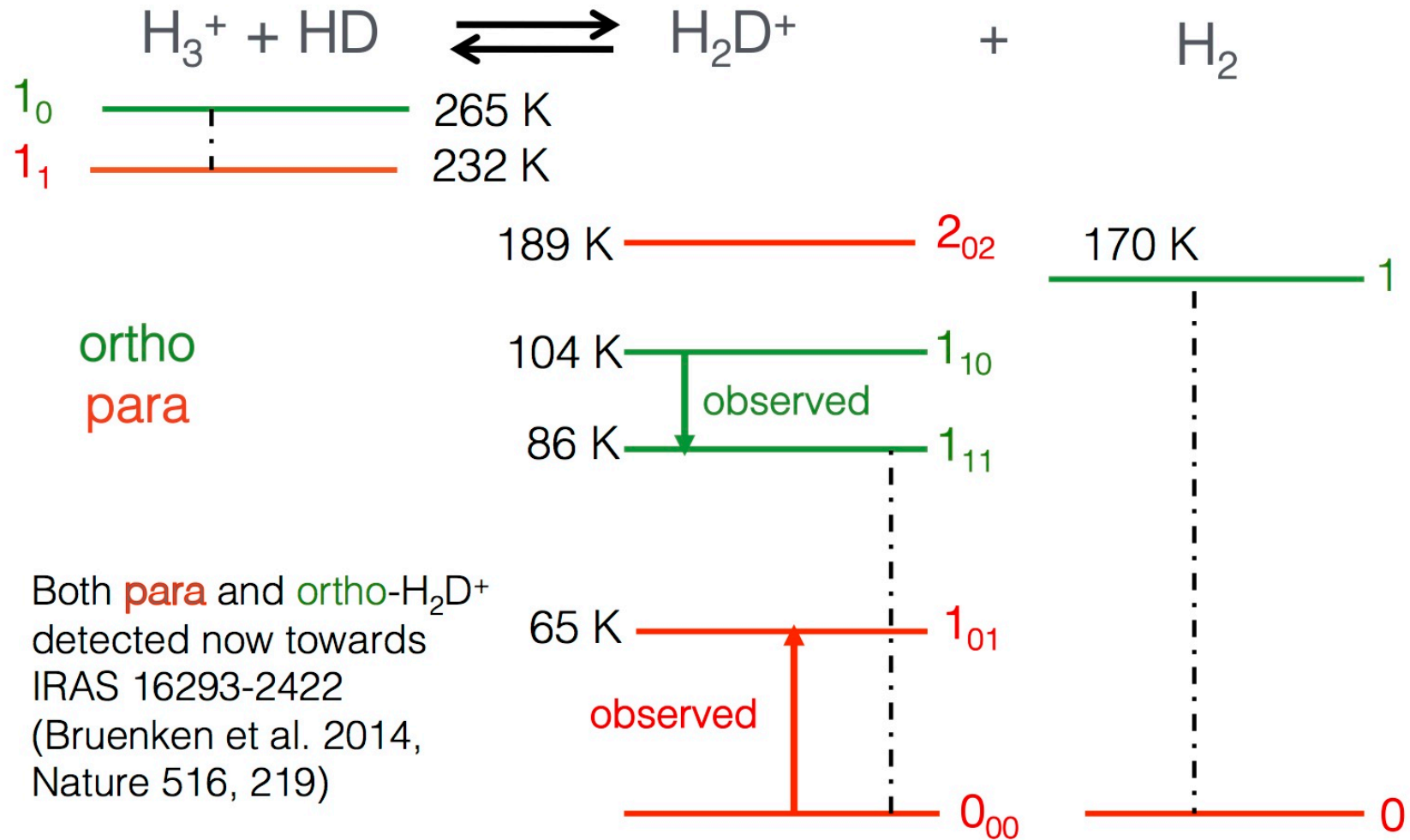
Energy difference btw **ortho** ($\uparrow\uparrow$)
and **para** ($\uparrow\downarrow$) H_2

→ At low T, **o- H_2** /**p- H_2** should decrease

→ **o- H_2** can overcome reaction barriers



State to state chemistry : example of $H_3^+ + HD$ exchange



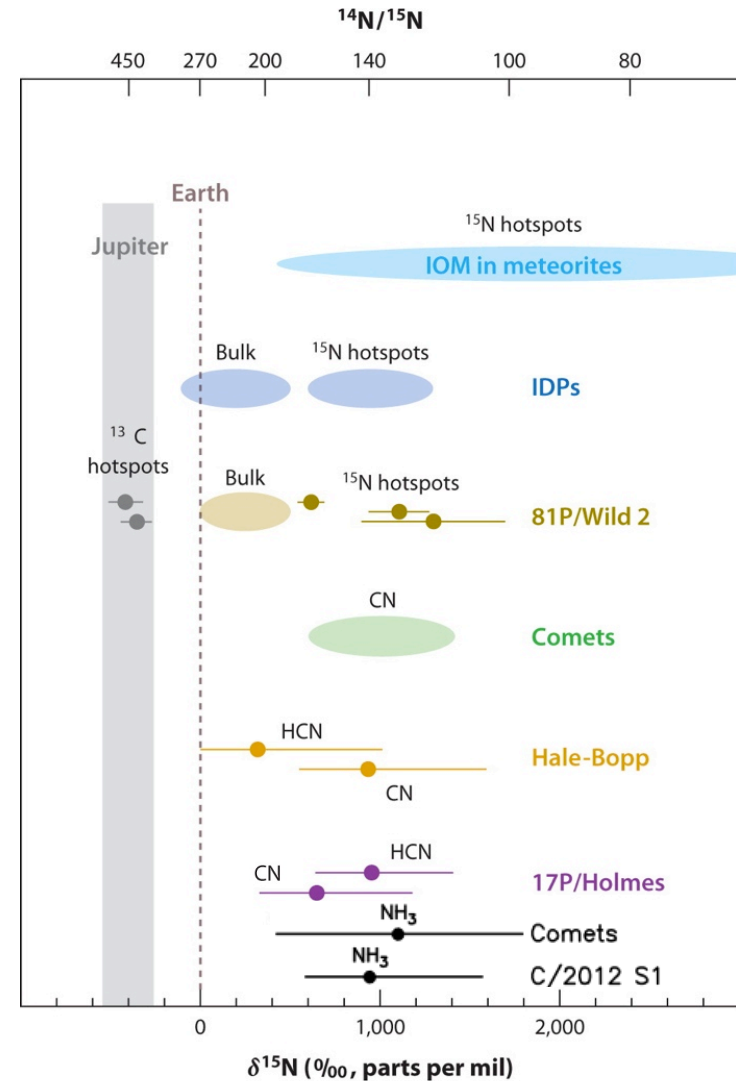
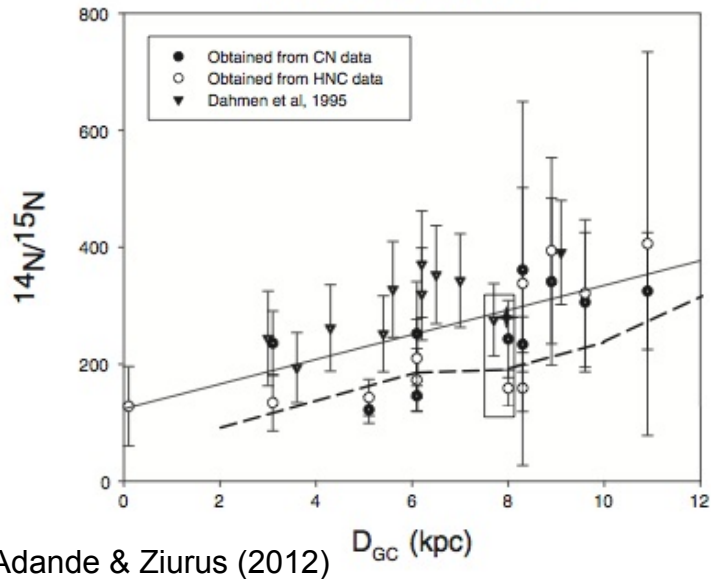
Slide from E. Roueff

Observed $^{14}\text{N}/^{15}\text{N}$

Protosolar ratio: ~ 440
(Marty et al. 2011)

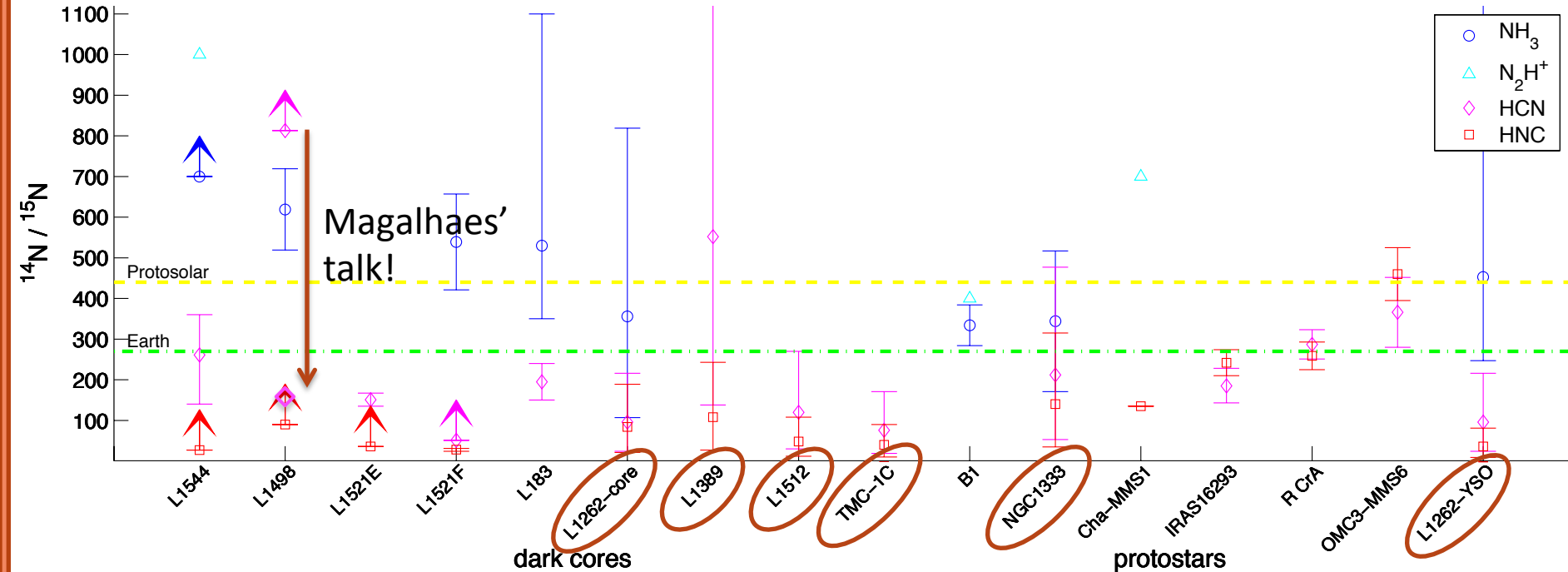
Most primitive reservoirs
enriched in ^{15}N

Interstellar ratios: wide range



Mumma & Charnley (2011) with NH_3 addition from Bockelée-Morvan et al. (2015)

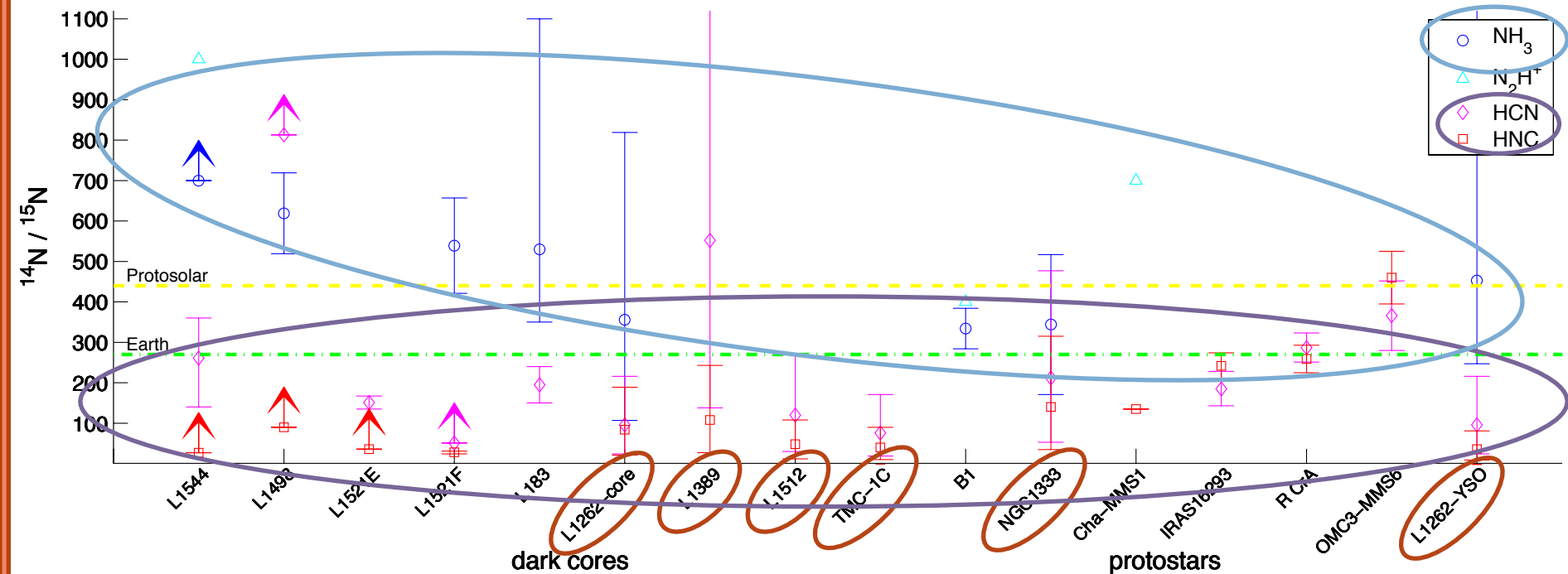
$^{14}\text{N}/^{15}\text{N}$ observations in dark cores



Hily-Blant P, et al. (2010). Bizzocchi L, et al. (2013). Milam, S. & Charnley, S. (2012). Gerin M, et al. (2009). Hily-Blant P, et al. (2013). Ikeda M, et al. (2002). Lis D.C, et al. (2010). Cordiner et al. In prep. Tennekes P.P., et al. (2006). Daniel et al. (2013). Wampfler S, et al. (2014). **Adande et al. in prep.**

Summary in Wirström et al., IAU XXIX General Assembly proc. Astronomy in Focus (2016)

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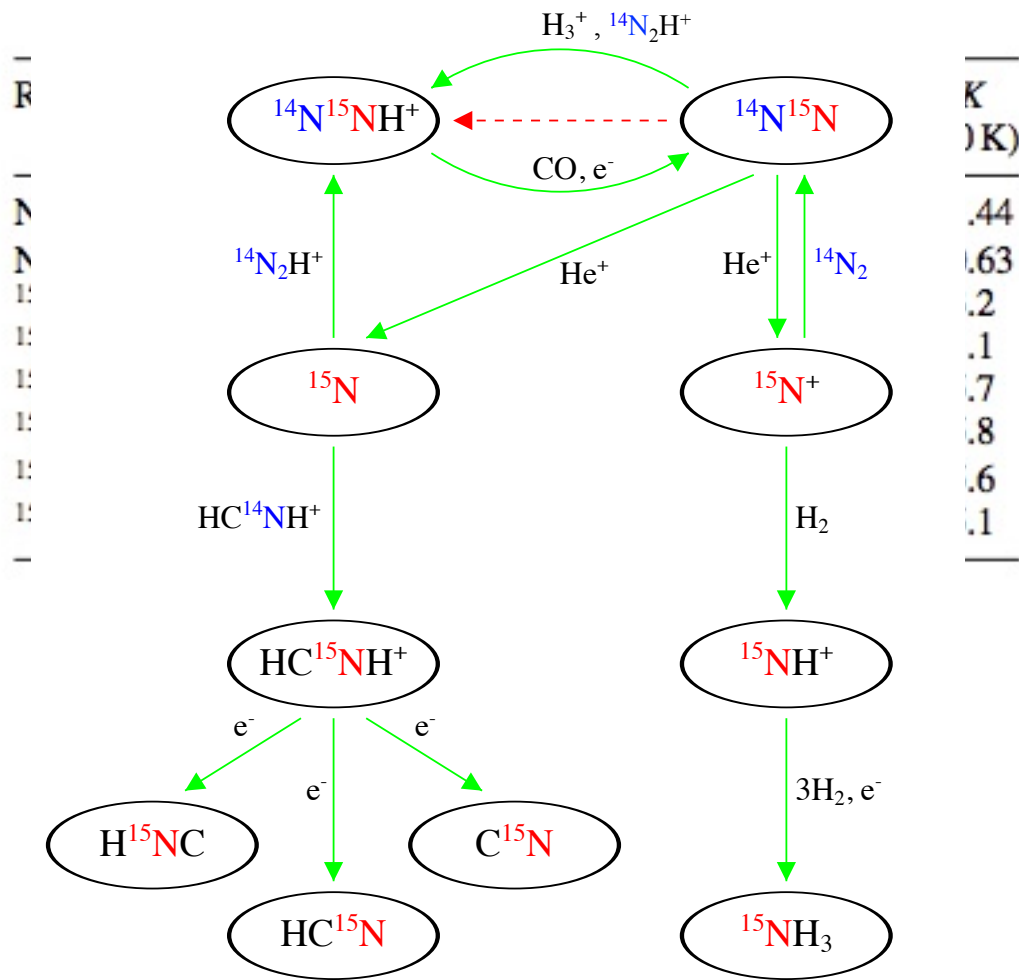
Interstellar nitrogen fractionation – models

Reaction	$f(B, m)$ (10 K)	$\Delta E_0/k$ (K)	K (10 K)
$\text{N}^{15}\text{N} + \text{HN}_2^+ \rightleftharpoons \text{N}_2 + \text{H}^{15}\text{NN}^+$	0.494	10.7	1.44
$\text{N}^{15}\text{N} + \text{HN}_2^+ \rightleftharpoons \text{N}_2 + \text{HN}^{15}\text{N}^+$	0.499	2.25	0.63
$^{15}\text{N}^+ + \text{N}_2 \rightleftharpoons \text{N}^+ + \text{N}^{15}\text{N}$	1.959	28.3	33.2
$^{15}\text{N}^+ + \text{NO} \rightleftharpoons \text{N}^+ + ^{15}\text{NO}$	0.979	24.3	11.1
$^{15}\text{N} + \text{CNC}^+ \rightleftharpoons \text{N} + \text{C}^{15}\text{NC}^+$	0.938	36.4	35.7
$^{15}\text{N} + \text{HN}_2^+ \rightleftharpoons \text{N} + \text{H}^{15}\text{NN}^+$	0.968	36.1	35.8
$^{15}\text{N} + \text{HN}_2^+ \rightleftharpoons \text{N} + \text{HN}^{15}\text{N}^+$	0.977	27.7	15.6
$^{15}\text{N} + \text{HCNH}^+ \rightleftharpoons \text{N} + \text{HC}^{15}\text{NH}^+$	0.968	35.9	35.1

Terzieva & Herbst (2000)

- Fractionation effect too minor to be detectable

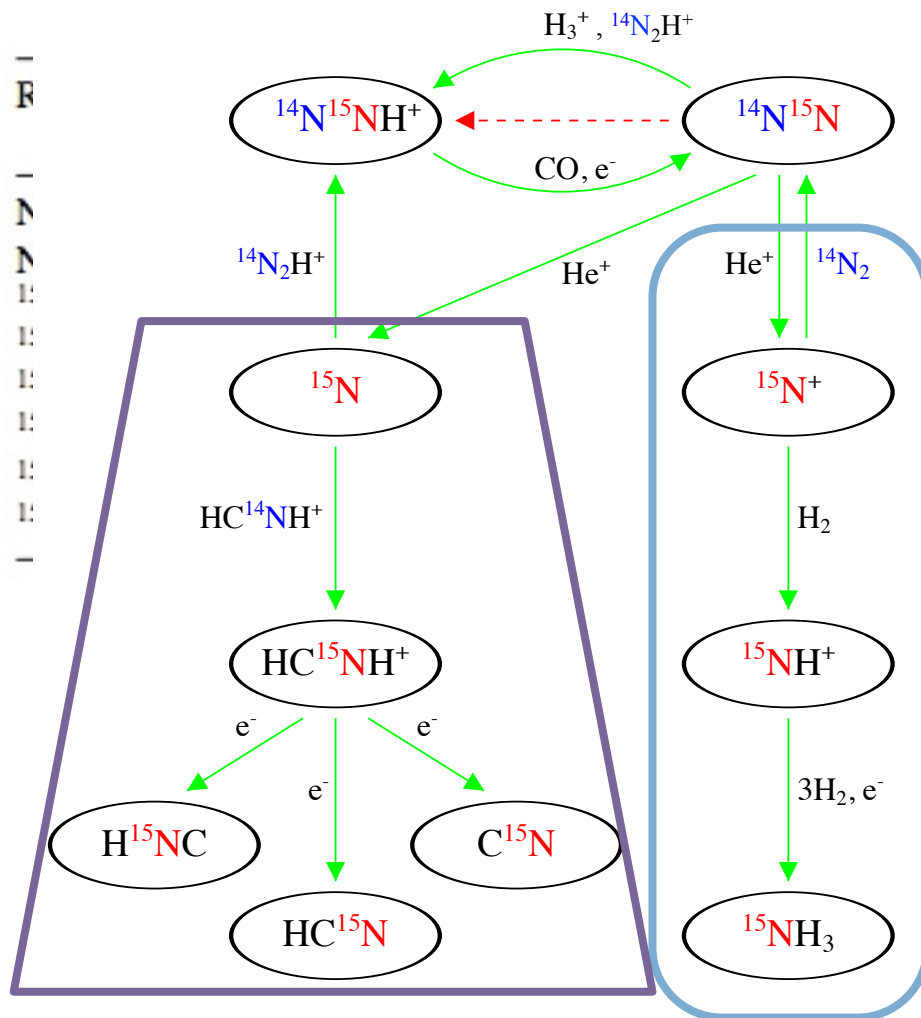
Interstellar nitrogen fractionation – models



Rodgers & Charnley (2008a,b)

- High density ($1\text{e}6\text{ cm}^{-3}$), CO depletion, and low temperature (10 K)
 ➔ $^{14}\text{N}/^{15}\text{N} \geq 50$
- Main ^{15}N pool: initially molecular (and atomic?)

Interstellar nitrogen fractionation – models



—
K
) (K)
—
.44
.63
.2
.1
.7
.8
.6
.1
—

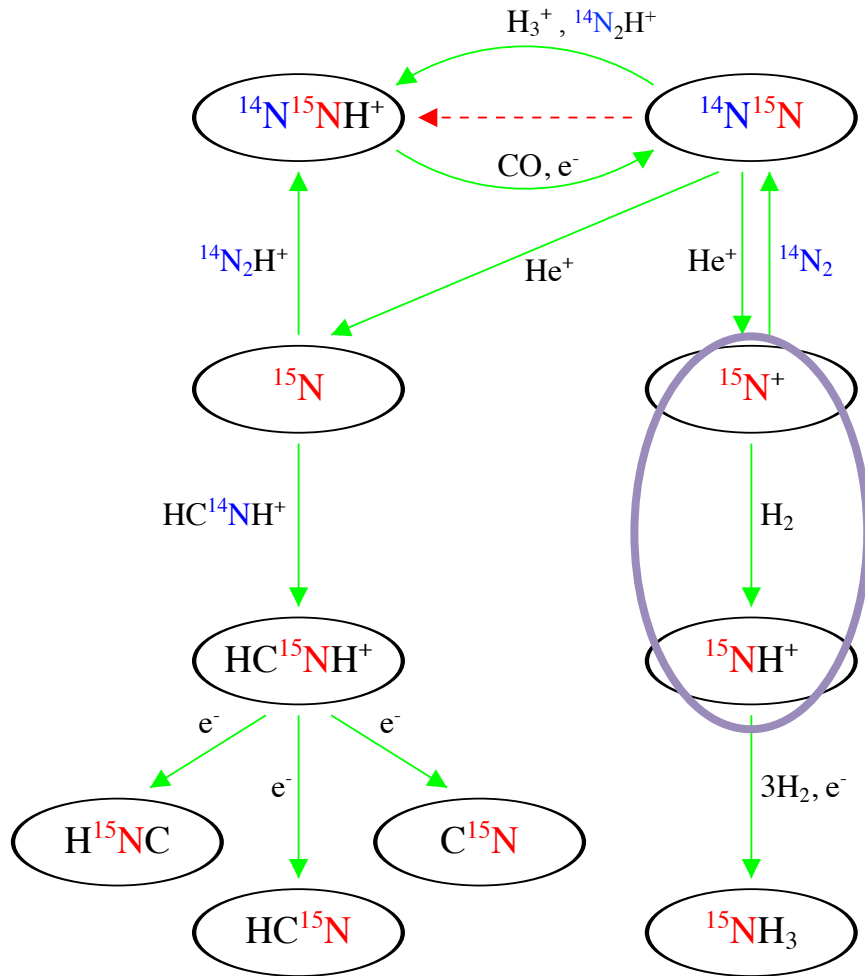
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➤ Main ^{15}N pool: initially
molecular (and atomic?)

➤ Separate ^{15}N routes for
Nitriles and **Amines**
➔ different fract. timescales

Interstellar nitrogen fractionation – models



—
K
) (K)
—
.44
.63
.2
.1
.7
.8
.6
.1
—

Wirström et al. (2012)



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

→ low o-H₂ suppress ¹⁵N fractionation in NH₃

- No effect on nitriles

→ More pronounced difference btw Nitriles and Amines

(also Hily-Blant et al., 2013)

N fractionation model results (before 2015)

THE ASTROPHYSICAL JOURNAL LETTERS, 757:L11 (5pp), 2012 September 20

WIRSTRÖM ET AL.

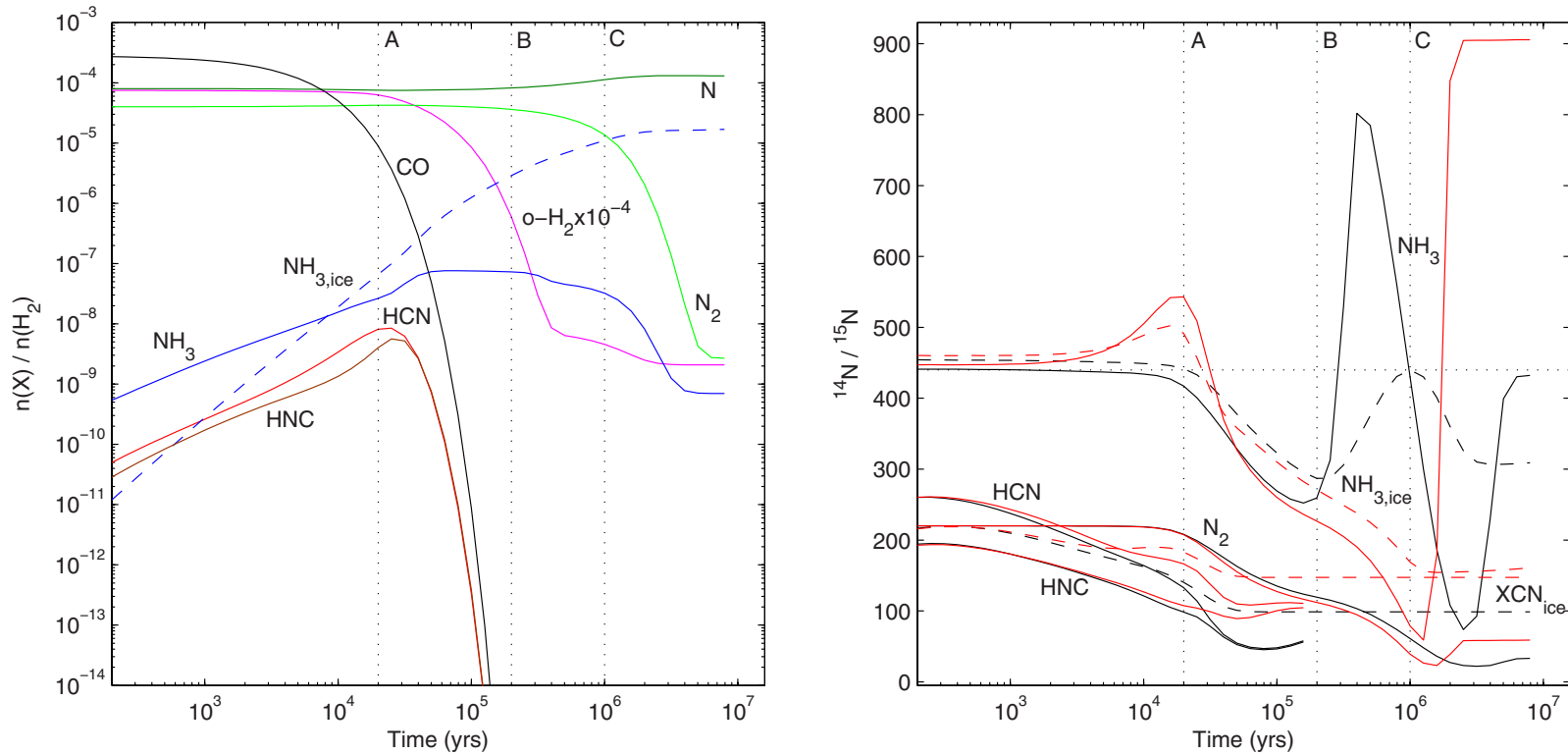
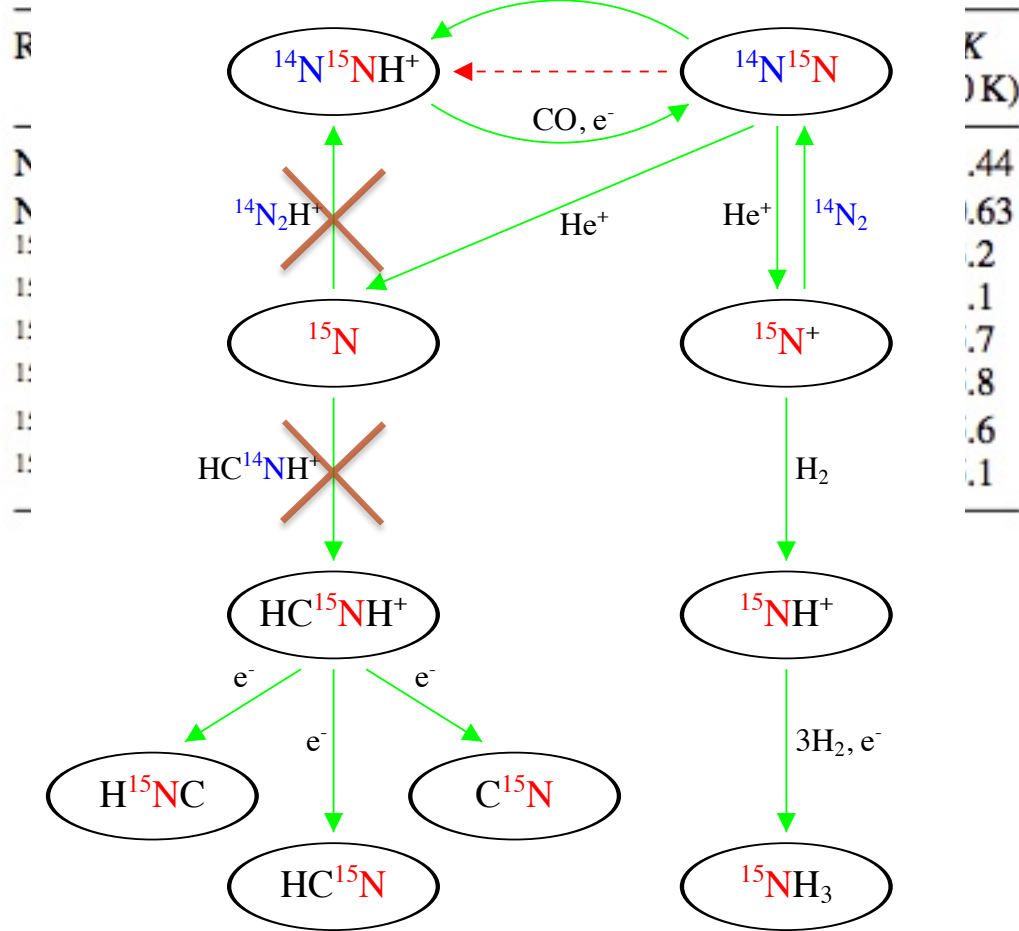


Figure 2. Left panel: time evolution of the nitrogen chemistry in dense cores, compared to CO and o-H_2 . Crucial times for the ^{15}N fractionation in nitrogen hydrides

Interstellar nitrogen fractionation – models

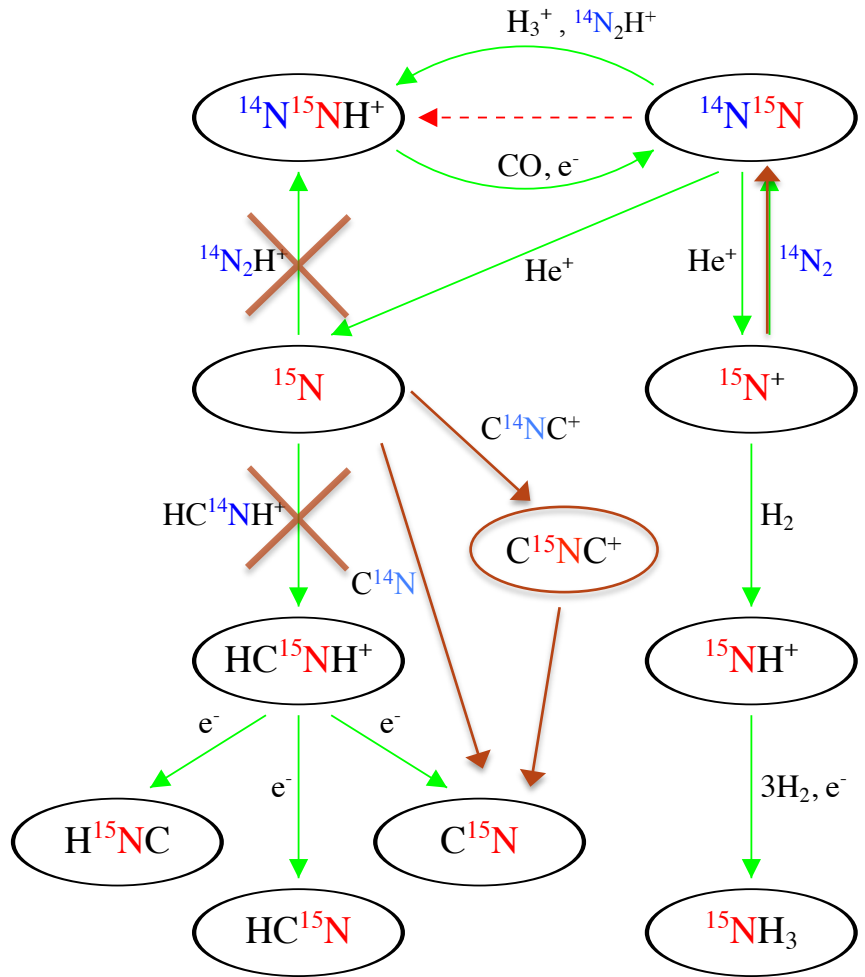


Roueff et al. (2015)

- Updated reaction rates based on ZPE's
- significant barriers in reactions suppress ^{15}N fractionation
- Demonstrates coupling btw N, C, and H fractionation

Interstellar nitrogen fractionation – models

F
N
E
E
E
E
E

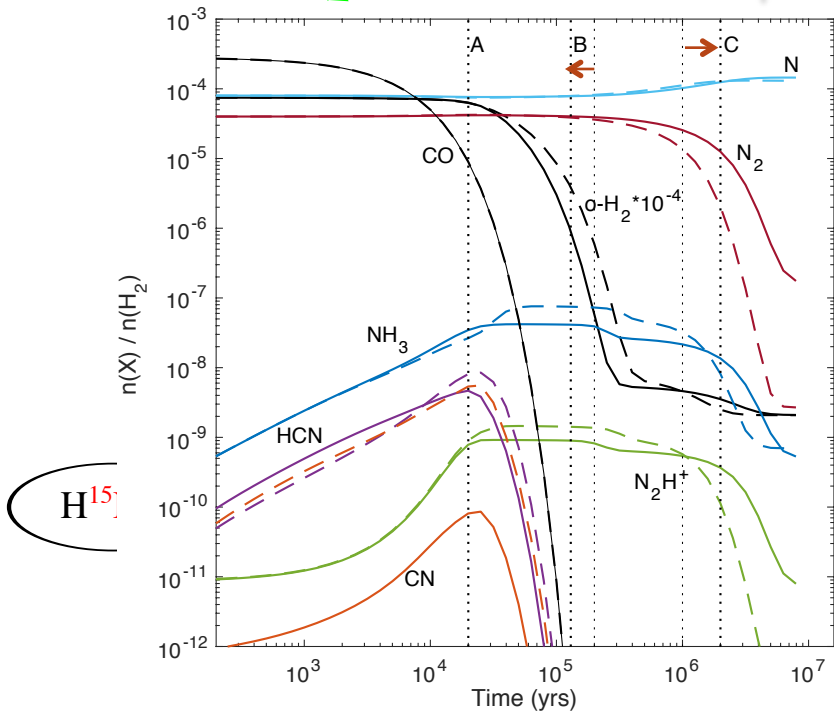
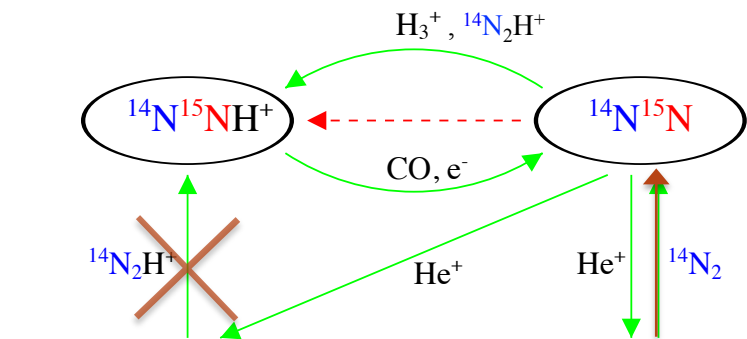


K
)K
0.44
0.63
0.2
0.1
0.7
0.8
0.6
0.1

Wirström et al. (2016, in prep)

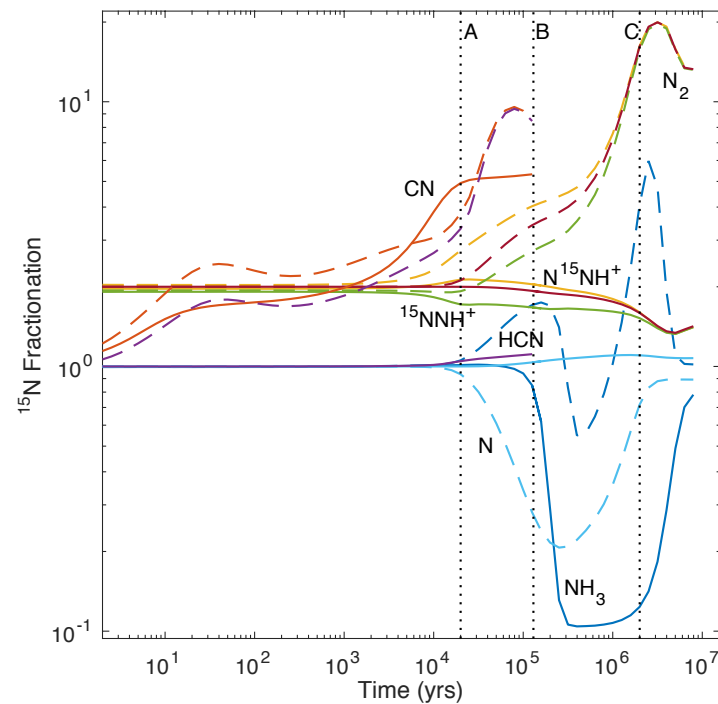
- Roueff' 15 N fractionation rates
- Updated N-chemistry (Wakelam, 2013)
- Including time-dependent H_2 OPR and freeze-out!

Interstellar nitrogen fractionation – models



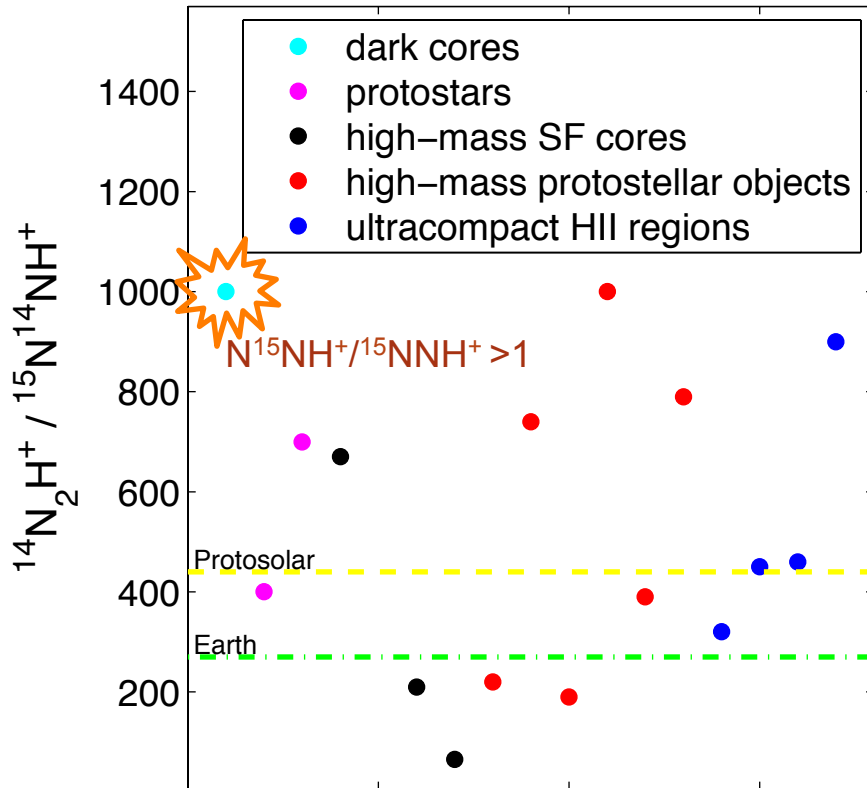
Wirström et al. (2016, in prep)

- Roueff'15 N fractionation rates



The N_2H^+ problem

Observations



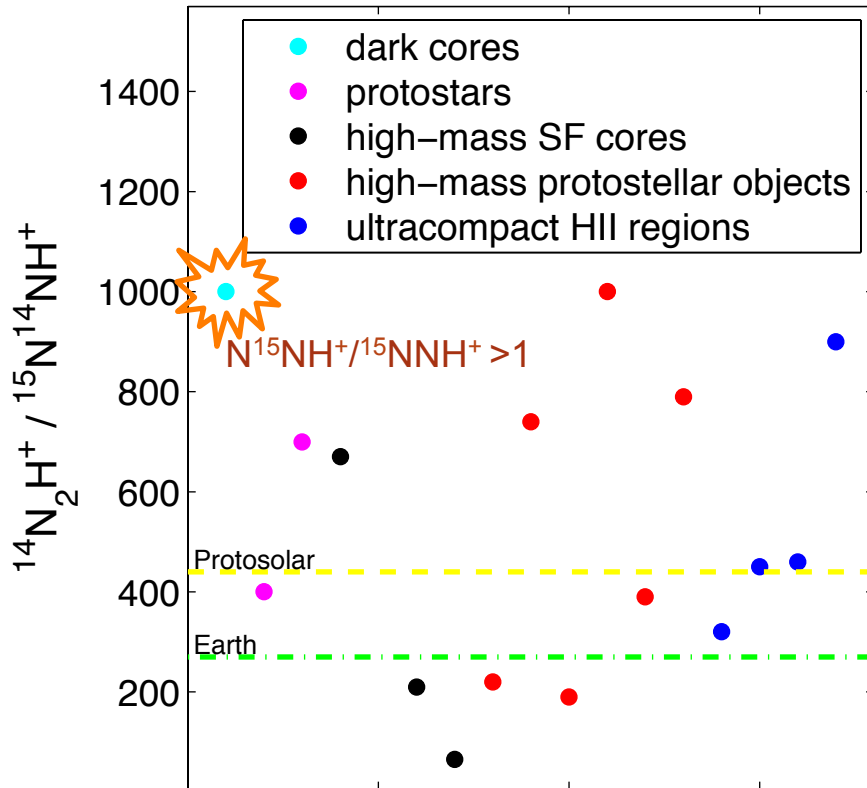
Bizzocchi L, et al. (2013). Daniel et al. (2013).
Cordiner et al. in prep. Massive SF sources:
Fontani et al. (2015).

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 \sim elemental
 - Dore et al (2016, subm): Incl. (optimistic) fractionation to $^{15}N_2$ and $^{15}N_2H^+$
- Even lower $^{14}N/^{15}N$ in N_2H^+

The N_2H^+ problem

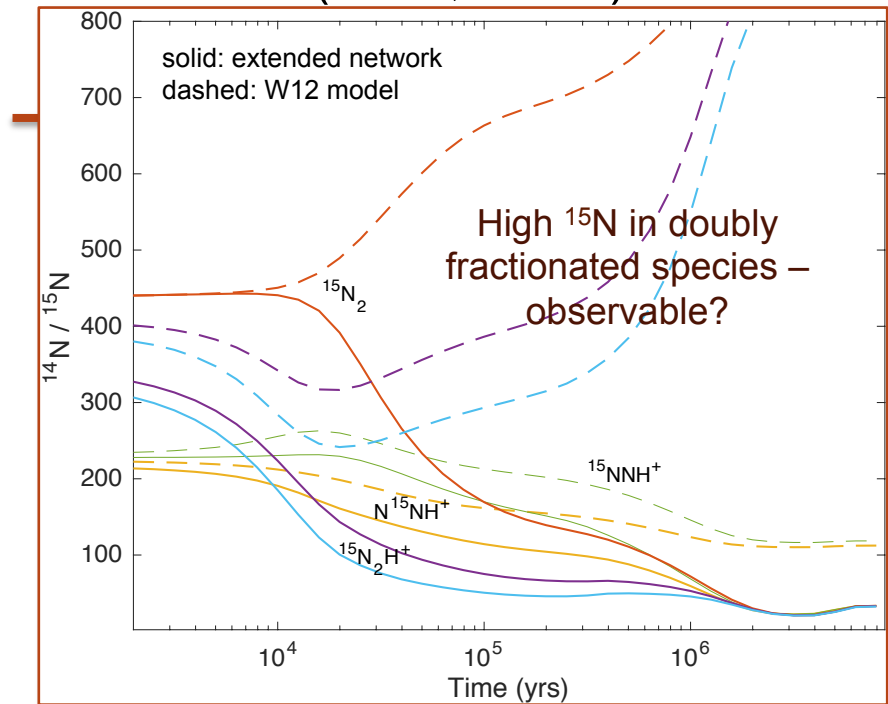
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- Dore et al (2016, subm): Incl.



Summary

- Disequilibrium ion-molecule chemistry under cold, dense cloud conditions lead to different ^{15}N fractions in nitriles and amines, in agreement with observations.
- A time-dependent H_2 OPR lead to high $^{14}\text{N}/^{15}\text{N}$ ratios in amines.
- New estimated rates for some of the relevant isotopic exchange reactions (Roeuff et al. 2015) suppress ^{15}N enhancements – **Barriers need to be re-evaluated for range of interaction geometries?**
- All current models fail to reproduce low observed ^{15}N in N_2H^+ in dark clouds – **Need to be addressed**
- Spectroscopy available for doubly ^{15}N substituted N_2H^+ – observations might provide further constraints
- Observations of ^{15}N fractionation in NH_3 and N_2 proxys in dark cores are complicated and scarce – need substantial sample of dark cores are crucial to obtain a complete picture of fractionation chemistry

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Funding by Swedish National
Space Board and NASA's
Origins of Solar Systems
Program

