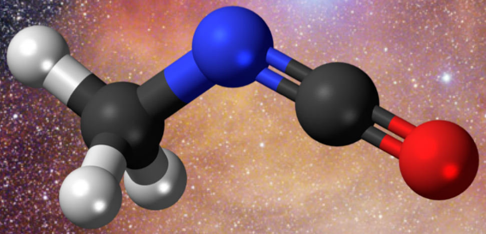
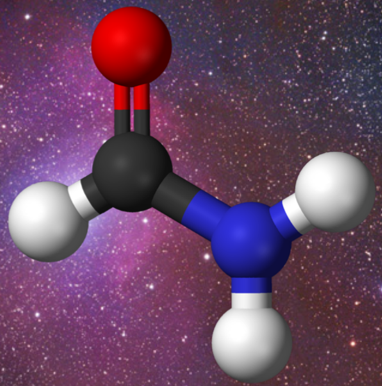
Chemical modelling of formamide and methyl isocyanate in star-forming regions





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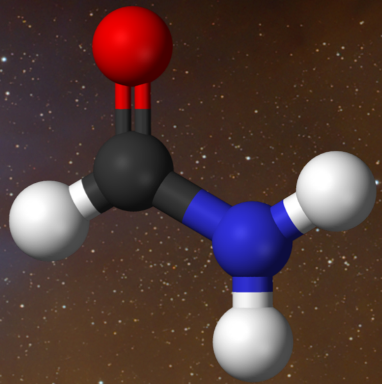
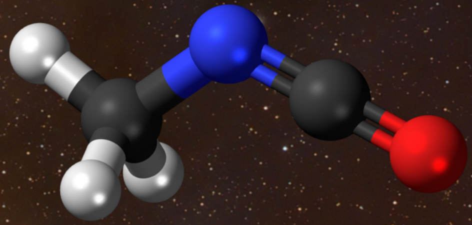
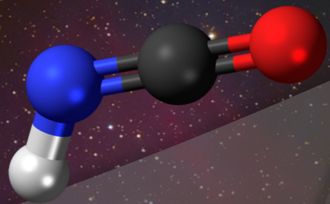
The search for pre-biotic species

The peptide bond: CO-NH

Important bond in biochemistry
(link between two amino-acids)

Several species detected with a peptide-like bond (e.g. NH_2CHO, CH_3NCO) or a peptide bond (HNCO)

The search for pre-biotic species

Glycine
(NH_2CH_2COOH)

Methylamine NH_2CH_3	Cyanamide NH_2CN	Aminoacetonitrile NH_2CH_2CN
Glycolaldehyde $HOCH_2CHO$	Methyl Formate $HCOOCH_3$	Acetic Acid CH_3COOH
Hydroxylamine NH_2OH	Acetamide NH_2COCH_3	Formamide NH_2CHO
N-Methyl Formamide N-CH_3NHCHO	Isocyanic Acid (+isomers) HNCO/HCNO/HOCN	Methyl Isocyanate CH_3NCO (+isomers)

➔ Understand the chemistry of glycine precursors and COM-related species.

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➔ Understand the chemistry of glycine precursors and COM-related species.

Modelling of NH_2CHO, CH_3NCO, HNCO (& isomers)

UCLCHEM (Viti et al. 2004; Holdship et al. 2017)

https://uclchem.github.io/

Gas-phase + dust grain chemical code (364 species; 3446 reactions)

Recently proposed gas-phase/grain-surface reactions for HNCO and CH_3NCO (+ isomers)

 # = grain surface

Reactions	Reference
Isocyanic Acid – HNCO/HOCN/HCNO	
Complex gas/grain network	Quan et al. (2010)
$\#NH + \#CO \longrightarrow \#HNCO$	Fedoseev et al. (2015)
Methyl Isocyanate – CH_3NCO	
$HNCO + CH_3 \longrightarrow CH_3NCO + H$	Halfen et al. (2015)
$\#CH_3 + \#OCN \longrightarrow \#CH_3NCO$	Belloche et al. (2017) ; Ligterink et al. (2017)
$\#CH_3 + \#HNCO \longrightarrow \#CH_3NCO + \#H$	Ligterink et al. (2017)
$\#CH_3 + \#HNCO \longrightarrow \#CH_4 + \#OCN$	Ligterink et al. (2017)
$\#CH_3NCO + \#H \longrightarrow \#CH_3NH + \#CO$	Ligterink et al., private communication

Quénard et al., (2018)

Modelling of NH_2CHO, CH_3NCO, HNCO (& isomers)

New theoretical calculations from Majumdar et al. (2018)

Reaction		α	β	γ
$HNCO + CH_3$	$\rightarrow CH_3NCO + H$	1.00×10^{-10}	0	8.04×10^3
$CH_3NCO + H_3^+$	$\rightarrow CH_3NCOH^+ + H_2$	1.00×10^{-9}	-0.5	0
$CH_3NCO + HCO^+$	$\rightarrow CH_3NCOH^+ + CO$	1.09×10^{-9}	-0.5	0
$CH_3NCO + H^+$	$\rightarrow CH_3NCO^+ + H$	1.00×10^{-9}	-0.5	0
$CH_3NCO + CO^+$	$\rightarrow CH_3NCO^+ + CO$	1.00×10^{-9}	-0.5	0
$CH_3NCO + He^+$	$\rightarrow CH_3NCO^+ + He$	1.00×10^{-9}	-0.5	0
$CH_3NCO^+ + e^-$	$\rightarrow CH_3 + OCN$	1.50×10^{-7}	-0.5	0
$CH_3NCOH^+ + e^-$	$\rightarrow CH_3NCO + H$	3.00×10^{-7}	-0.5	0
CH_3NCO + CRP	$\rightarrow CH_3 + OCN$	4.00×10^3	0	0
CH_3NCO + Photon	$\rightarrow CH_3 + OCN$	5.00×10^{-10}	0.0	0
HCN + s-CO	→ s-HCN...CO	1	0	0
s-HCN...CO + s-H	→ s-H_2CNCO	1	0	2.40×10^3
s-H_2CNCO + s-H	→ s-CH_3NCO	1	0	0
s-CH_3 + s-HNCO	→ s-CH_3NCO	1	0	8.04×10^3
s-CH_3 + s-OCN	→ s-CH_3NCO	1	0	0
s-CH_3 + s-OCN^-	→ s-CH_3NCO + e^-	0	0	0
s-N + s-CH_3CO	→ s-CH_3NCO	1	0	0

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s-N + s-CH_3CO	→ s-CH_3NCO	1	0	0

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$s\text{-}CH_3 + s\text{-}OCN$	$\rightarrow s\text{-}CH_3NCO$	1	0	0
$s\text{-}N + s\text{-}CH_3CO$	$\rightarrow s\text{-}CH_3NCO$	1	0	0

Modelling of NH_2CHO, CH_3NCO, HNCO (& isomers)

Recently proposed gas-phase/grain-surface reactions for NH_2CHO

Reactions	Reference
Formamide – NH_2CHO	
$NH_2 + H_2CO \longrightarrow NH_2CHO + H$	Skouteris et al. (2017)
$\#HNCO + \#H \longrightarrow \#NH_2 + \#CO$	Song & Kästner (2016)
$\#HNCO + \#H \longrightarrow \#H_2NCO$	Song & Kästner (2016)
$\#H_2NCO + \#H \longrightarrow \#NH_2CHO$	Song & Kästner (2016)
$\#H_2NCO + \#H \longrightarrow \#HNCO + \#H_2$	Noble et al. (2016)
$\#NH_2 + \#HCO \longrightarrow \#NH_2CHO$	Fedoseev et al. (2016)
$\#NH_2 + \#HCO \longrightarrow \#NH_3 + CO$	Fedoseev et al. (2016)
$\#NH_2 + \#H_2CO \longrightarrow \#NH_2CHO + \#H$	Fedoseev et al. (2016)
$\#NH_2 + \#H_2CO \longrightarrow \#NH_3 + \#HCO$	Fedoseev et al. (2016)
$\#H_2NCO + \#CH_3 \longrightarrow \#CH_3CONH_2$	Belloche et al. (2017)
$\#NH_2CHO + \#OH \longrightarrow \#H_2NCO + \#H_2O$	Belloche et al. (2017)
$\#NH_2CHO + \#CH_2 \longrightarrow \#CH_3CONH_2$	Belloche et al. (2017)

Quénard et al., (2018)

Observational constraints

COMs in the pre-stellar core L1544

O-bearing and N-bearing COMS are more abundant at r~4000 AU (methanol peak position) (Jiménez-Serra et al. 2016)

Important non-detections:

Core centre	Methanol peak
X [NH_2CHO] < 2.4×10^{-13}	X [NH_2CHO] < 6.7×10^{-13}
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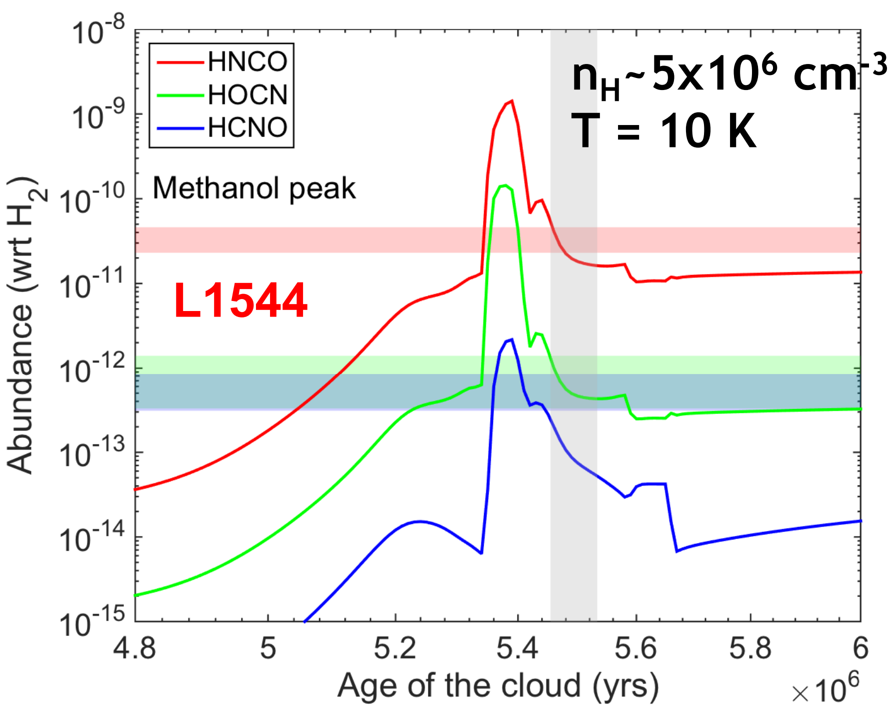
IRAS16293-2422: hot corino and envelope

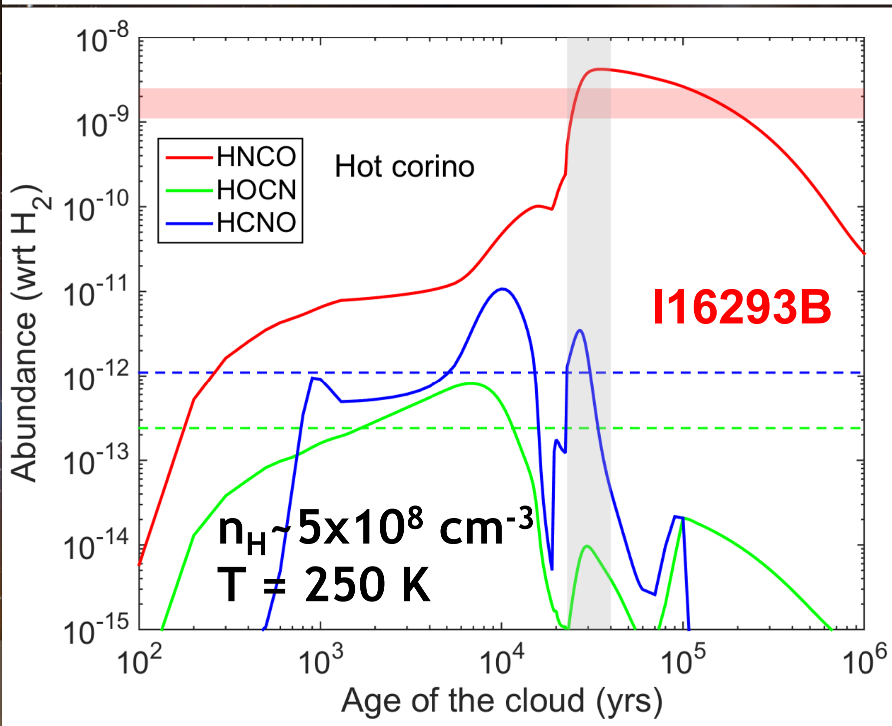
Recent detection of CH_3NCO toward the hot corino B!
(Martín-Doménech et al. 2017, Ligterink et al. 2017)
+
NH_2CHO observation from
Jaber et al. (2014) and Lopéz-Sepulcre et al. (2015)

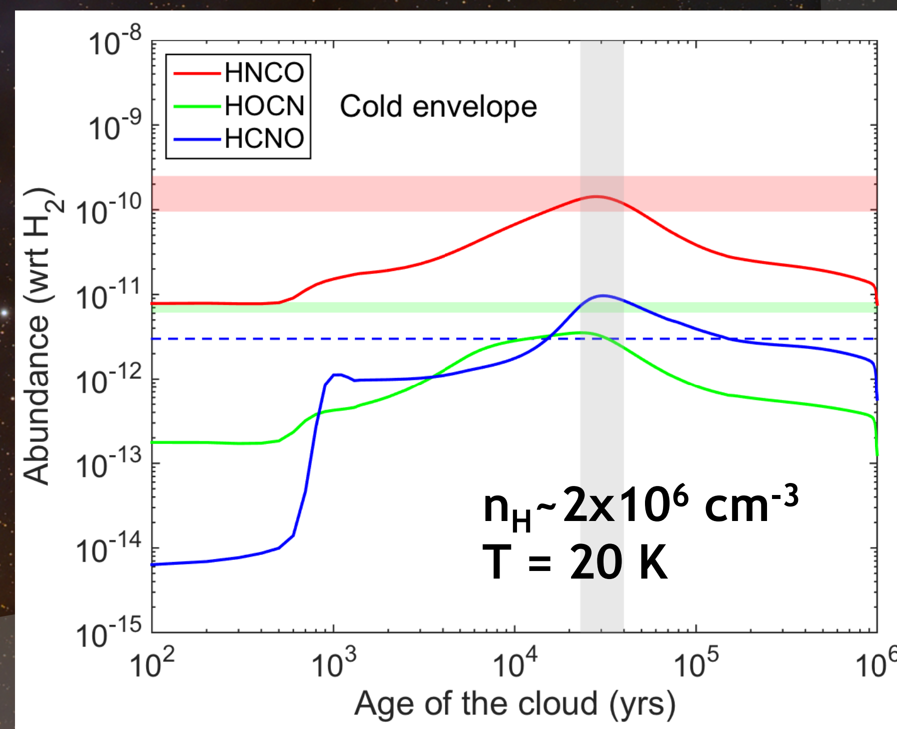


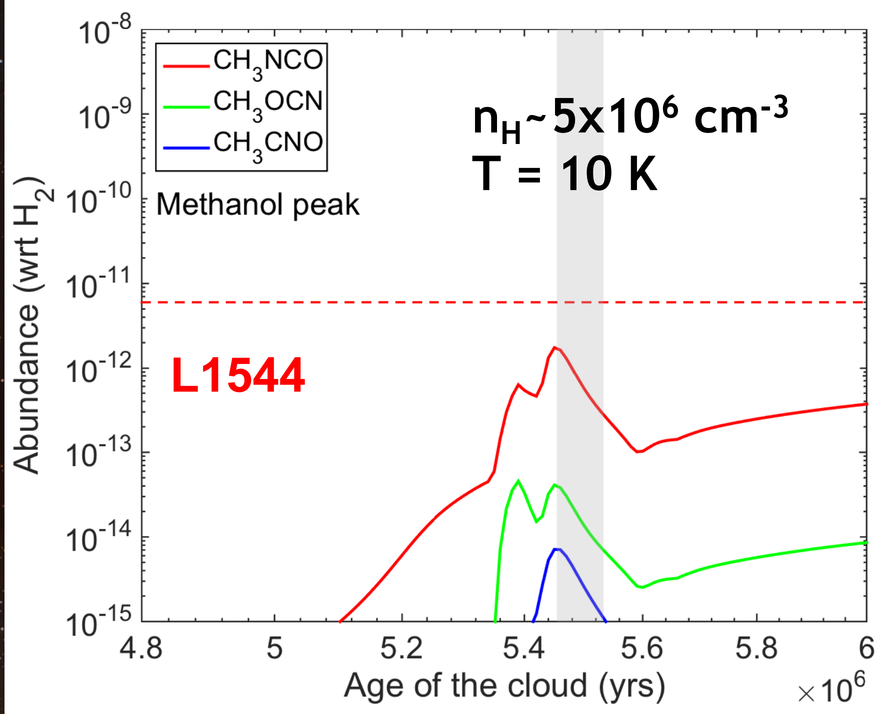
L1544 → t ~ 5.5 x 10^6 yr

IRAS16293 → Same chemical age used for both positions: t ~ 3 x 10^4 yr

Good agreement for HNCO in all three regions







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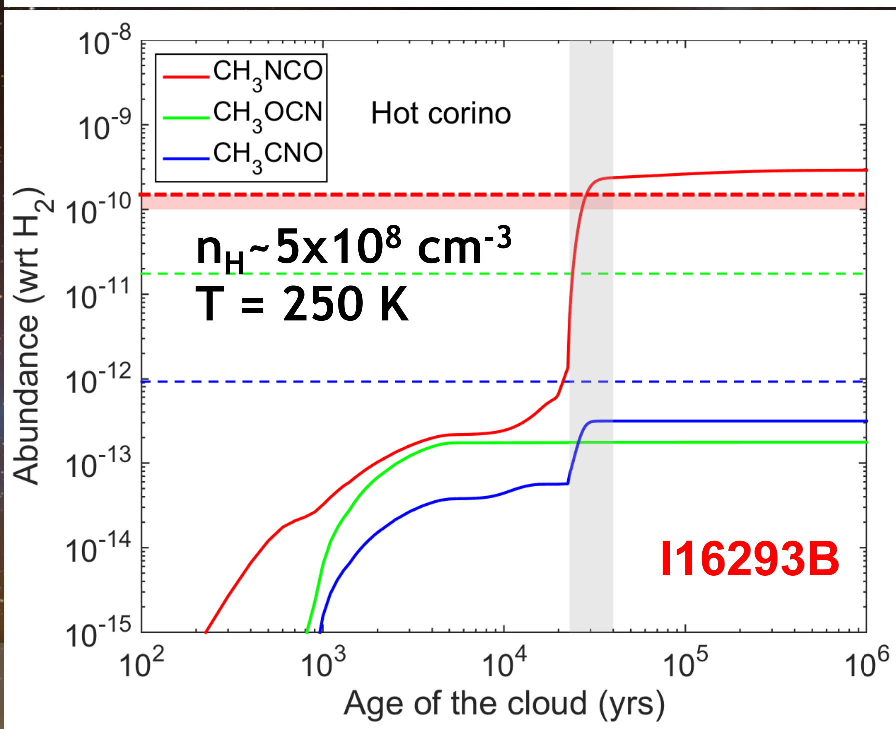

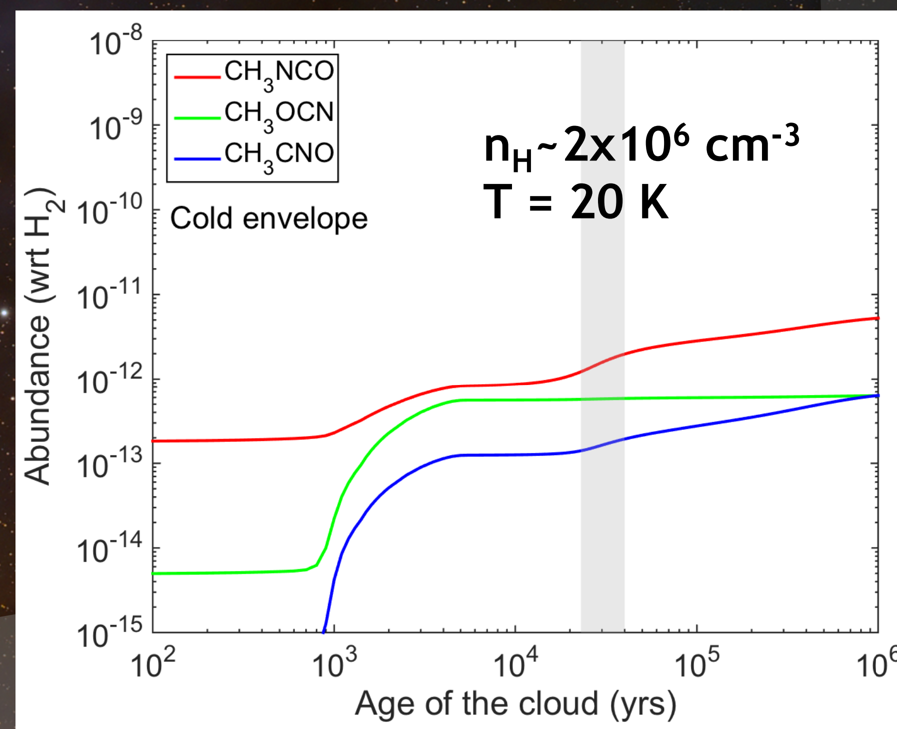

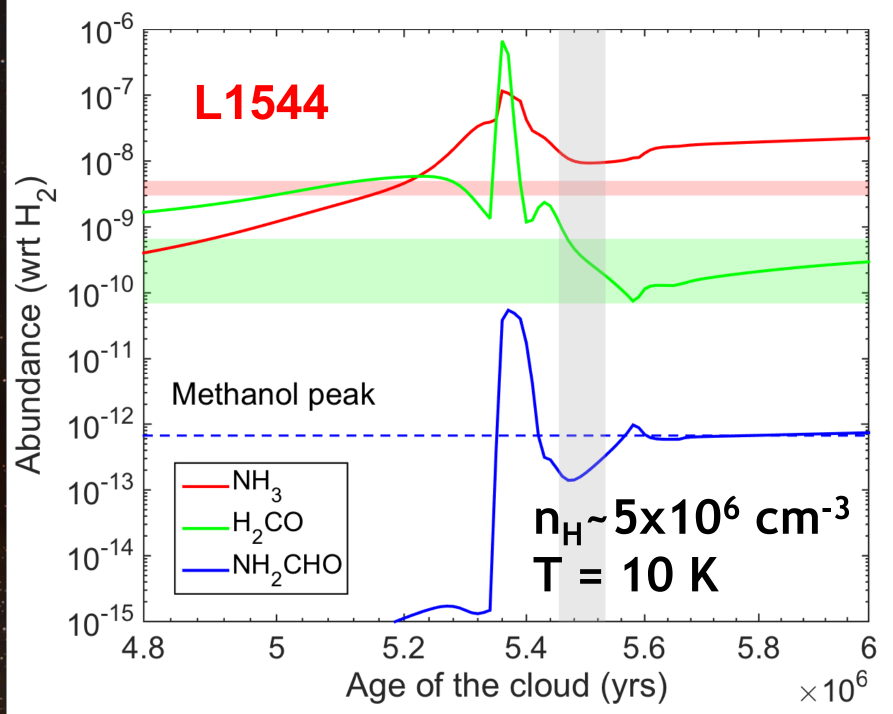

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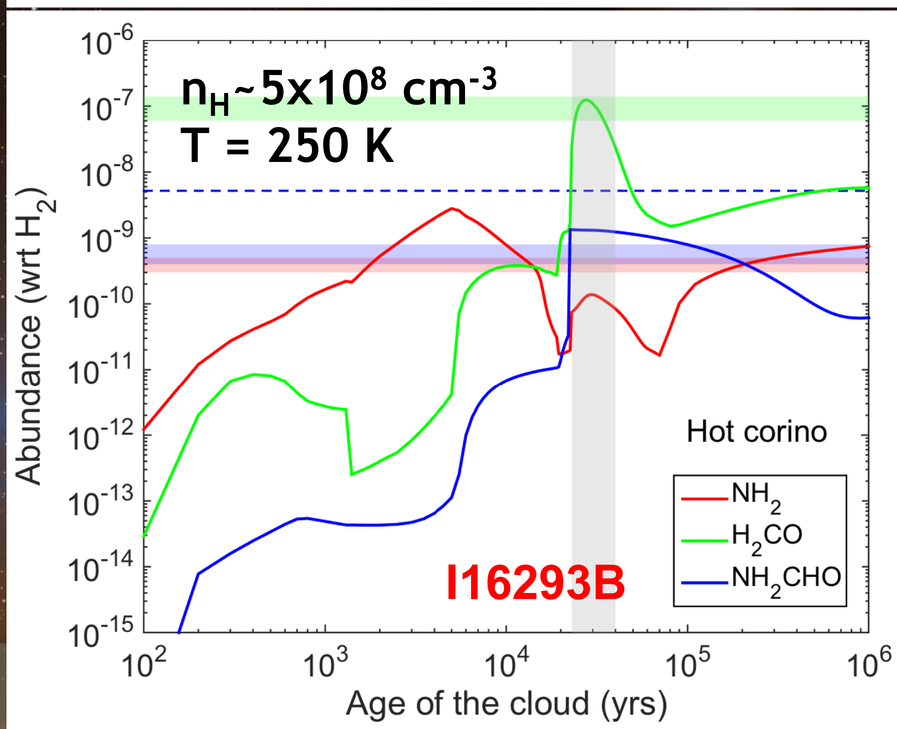
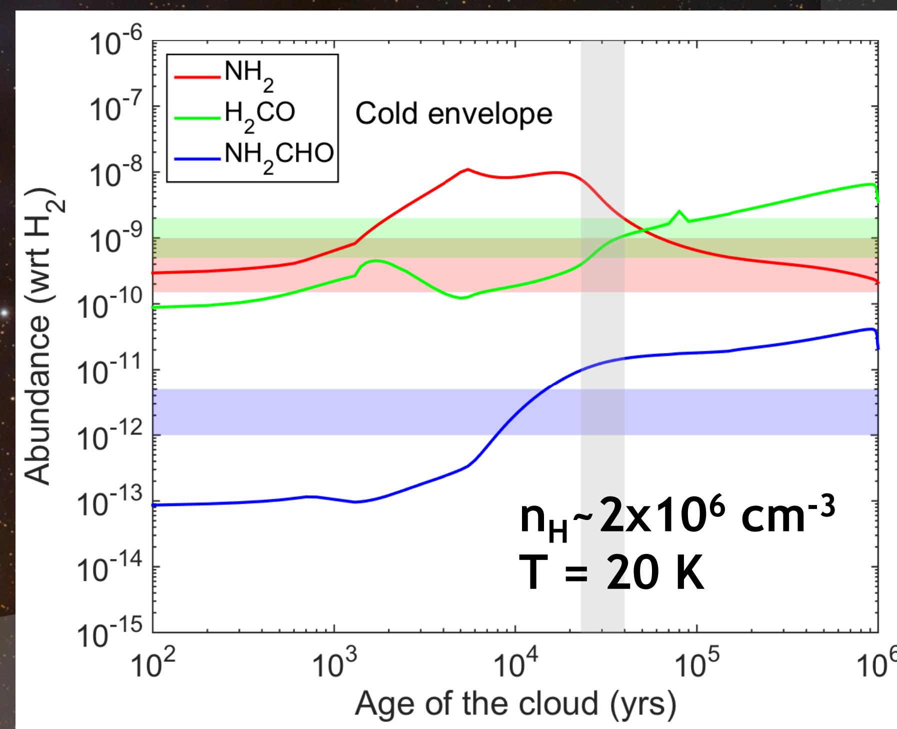
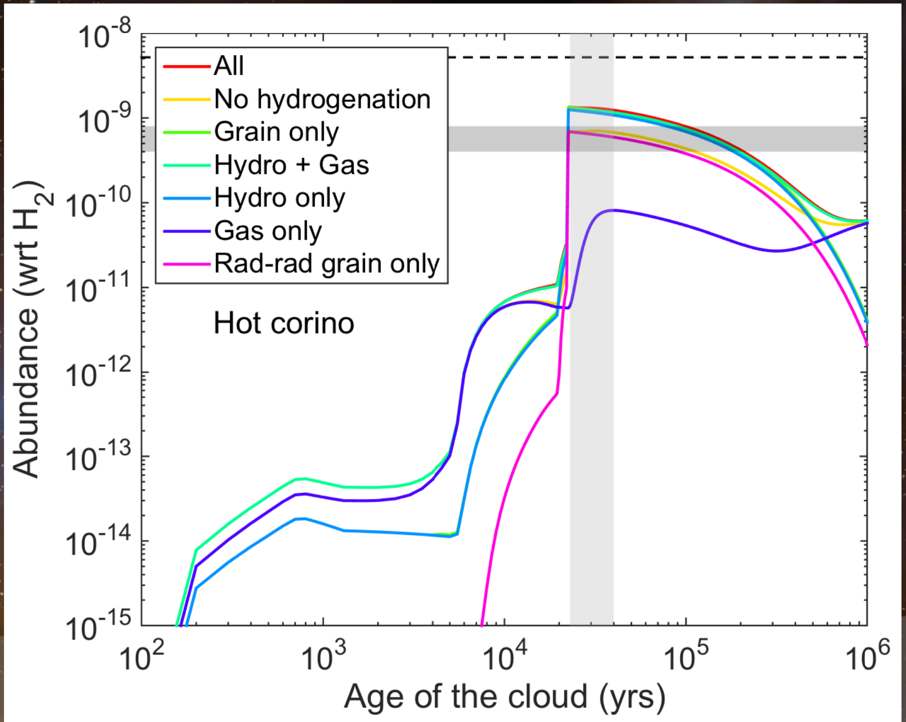




NH_2CHO chemistry

- **Gas phase chemistry**
- **Grain surface chemistry:**
  - **Radical-radical reactions**
  - **Hydrogenation**



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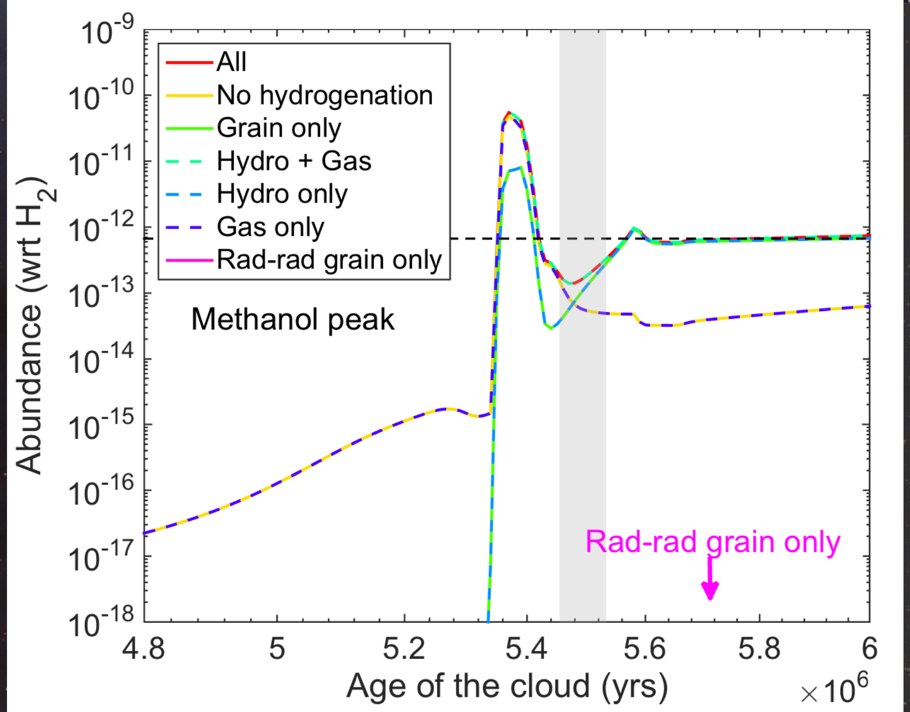

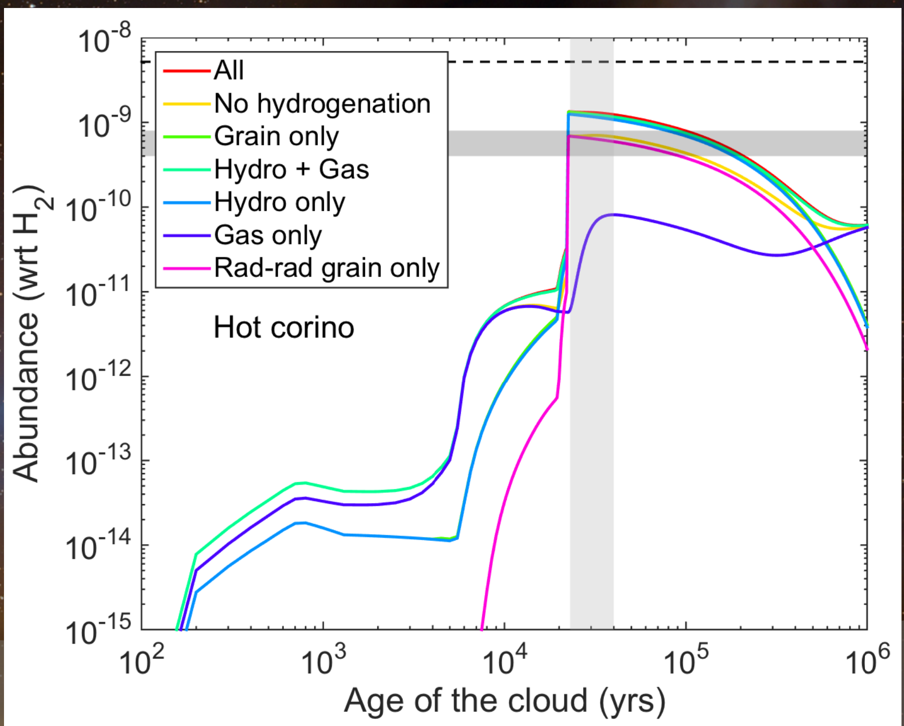

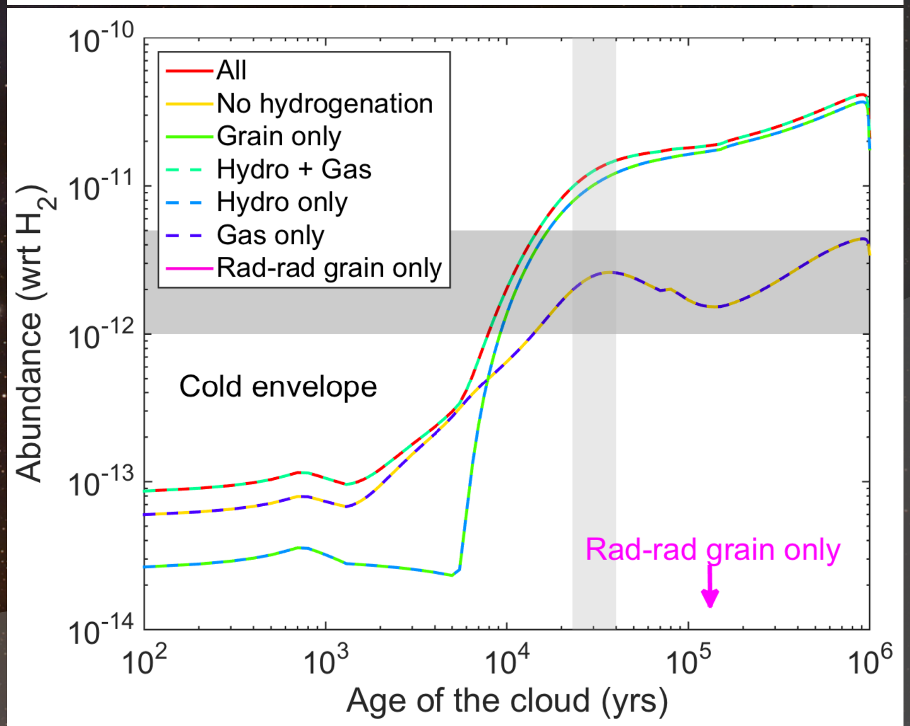

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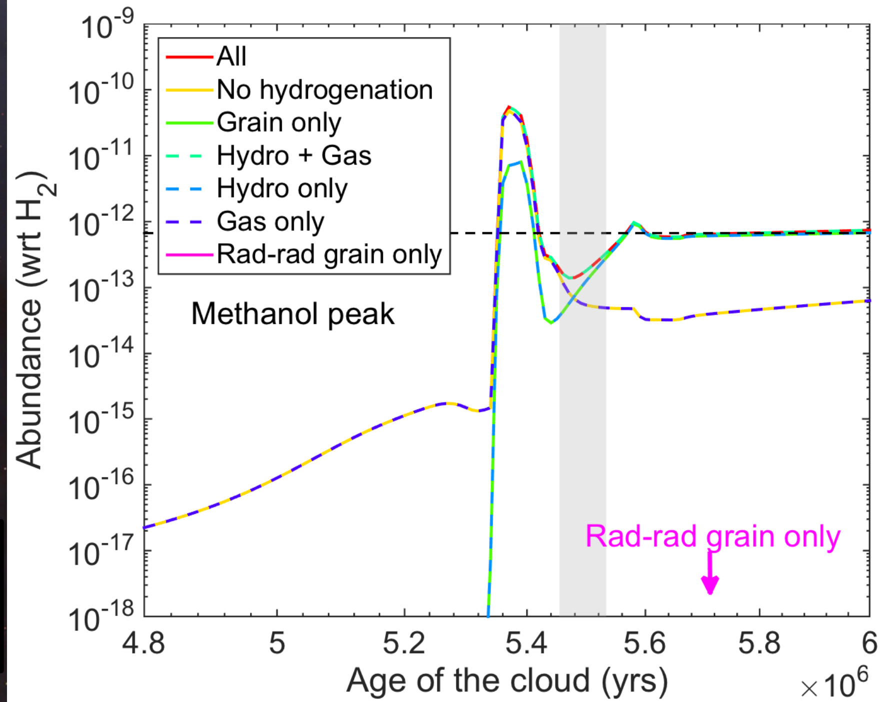
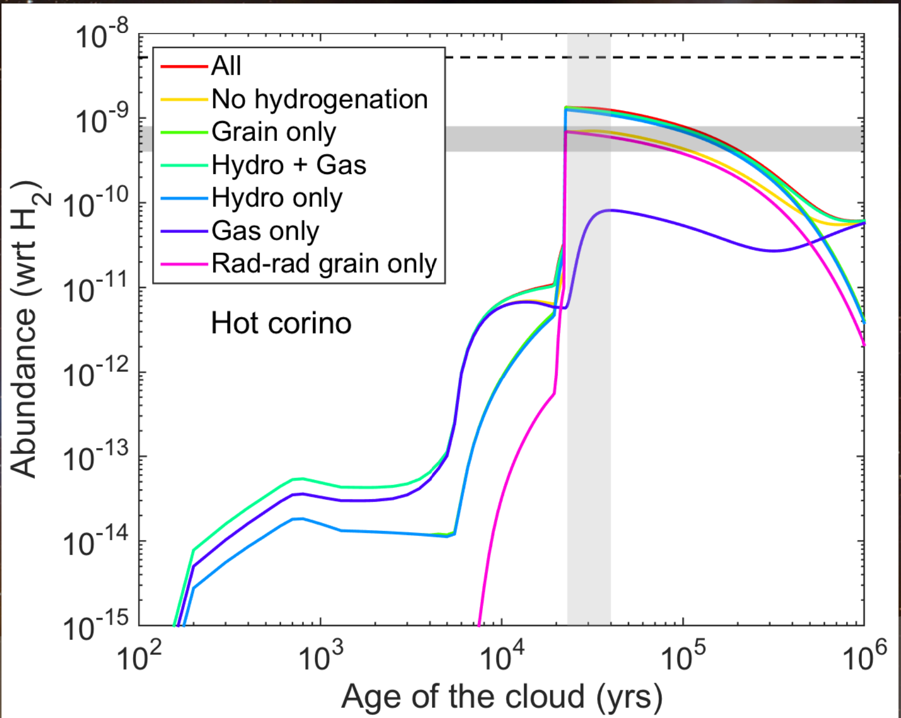
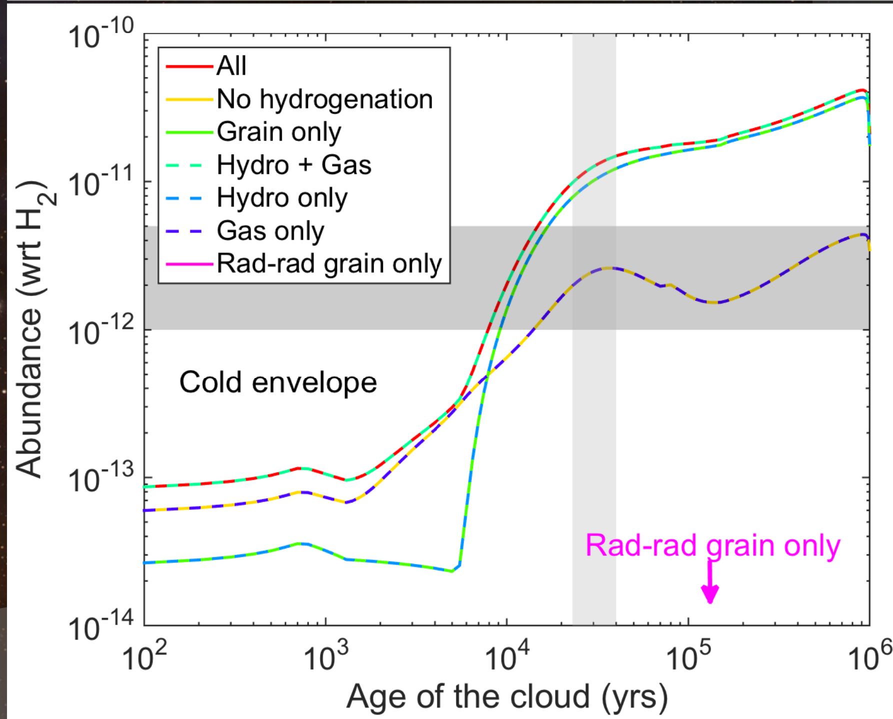
Modelling different physical regimes help to constrain the chemistry !



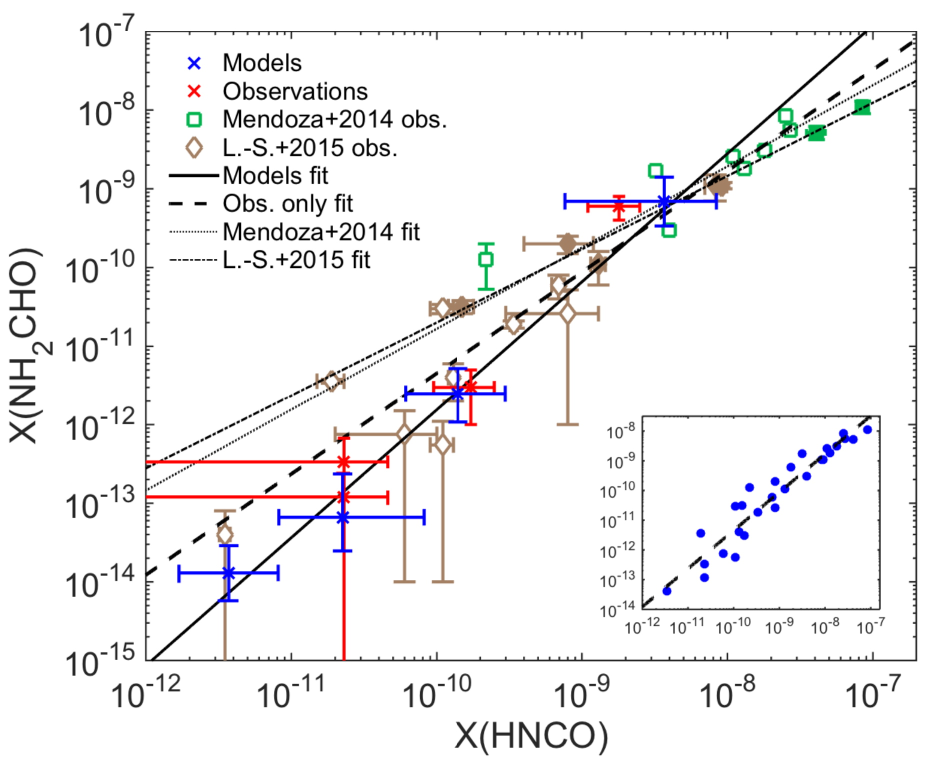


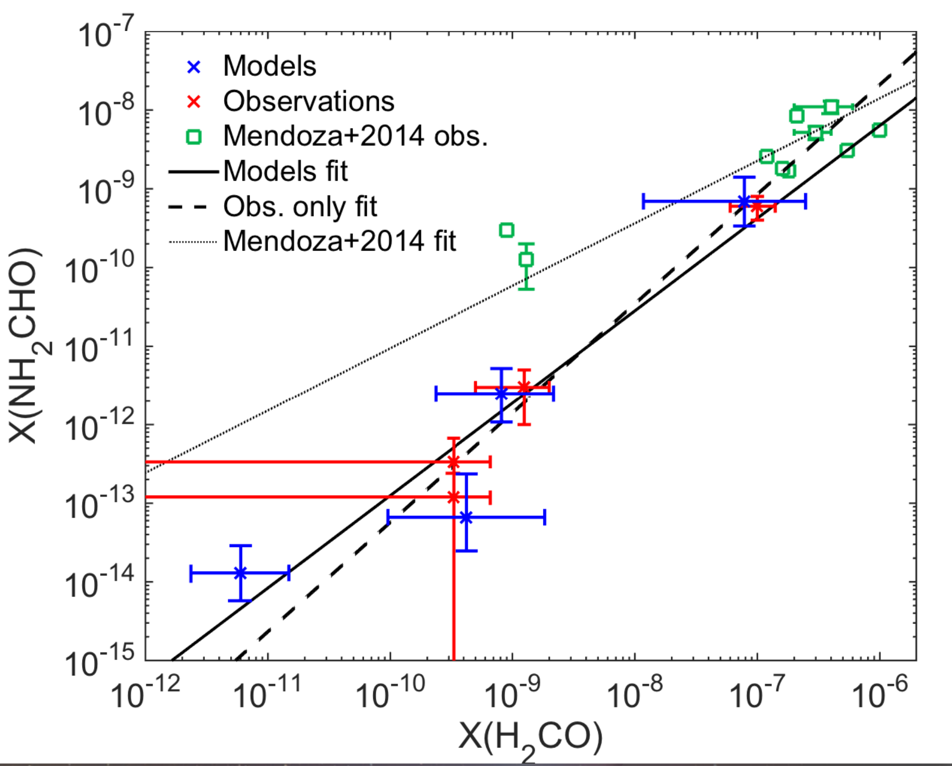


HNCO & H_2CO vs NH_2CHO

Mendoza et al. (2014) and **Lopéz-Sepulcre et al. (2015)**:
Observational correlation ➔ **Chemical correlation** between the two?

Modelling of NH_2CHO (no hydrogenation from HNCO)
➔ **Physical (environmental) correlation** depending mainly on the **temperature** that triggers different **chemical processes.**





Conclusions

- Modelling of N-bearing COMs predicts abundances of NH_2CHO, CH_3NCO (and isomers), HNCO (and isomers) in L1544 and IRAS16293 B
  - L1544: methanol peak
  - IRAS16293 B: hot corino and cold envelope

- Both gas-phase and grain-phase chemistry are needed to explain the observed abundances of NH_2CHO
  - Hydrogenation of HNCO tends to overestimate the NH_2CHO abundance compared to radical-radical reactions

- The observed correlation between HNCO and NH_2CHO may come from an environmental correlation (temperature) rather than a chemical correlation