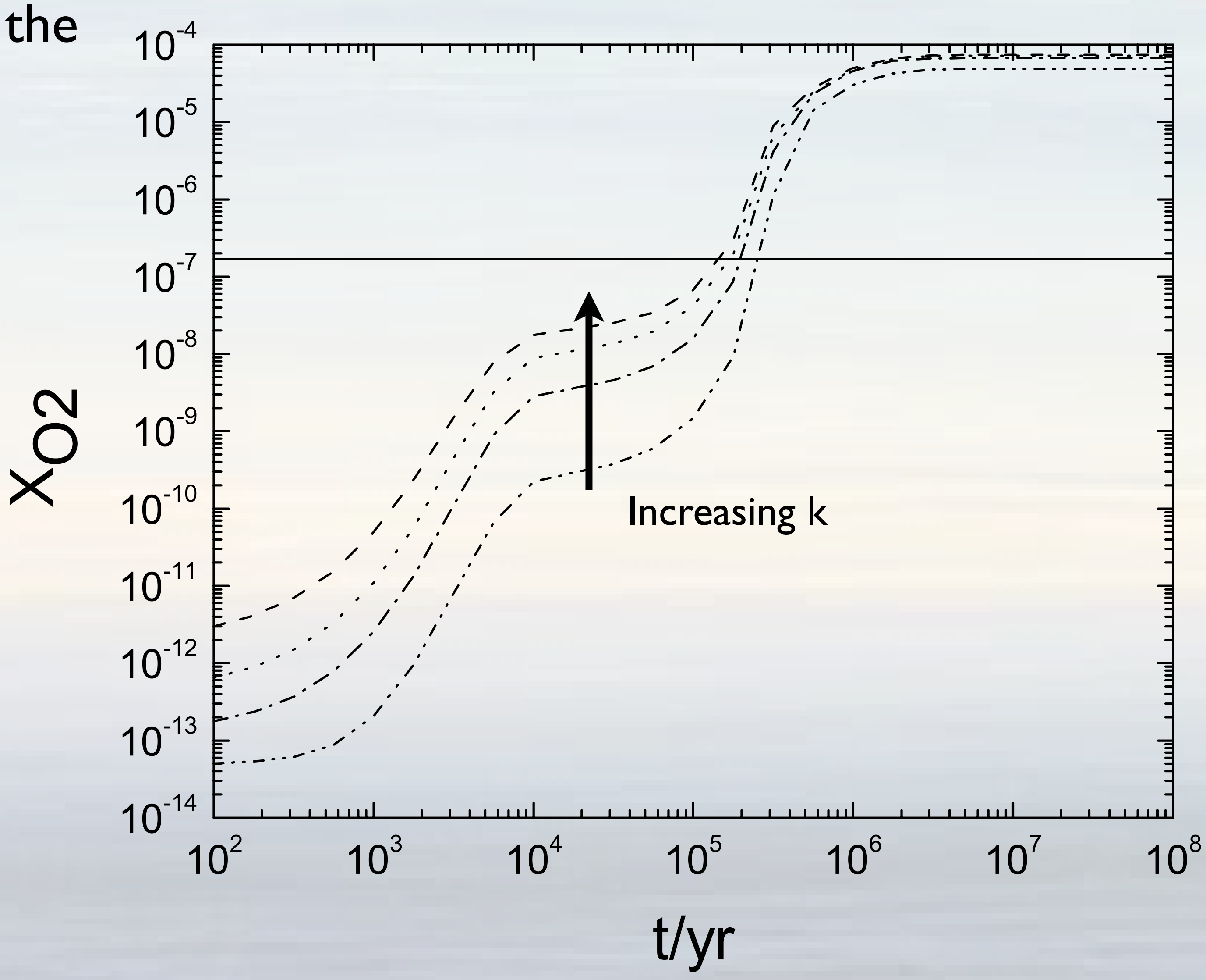
Selection of important reactions

What is an important reaction?

A reaction that form and destroy the most a species - does not mean that improving/changing its rate coefficient will change the abundance of the species.

Ex: main reaction of O_2 formation O + OH → O_2 + H (k)

But if you remove it, it can strongly change the abundance (see OCS later).



Quan, Herbst et al. (2008)

What is an important reaction?

In the context of this work: important reaction = change in its rate coefficient (by more than a factor of 2) changes model predictions

It might be direct relation: example of HC_5N

main reaction forming HC_5N: $C_5H_2N^+ + e^- \rightarrow HC_5N + H$
"important" reaction using sensitivity analysis: $C_5H_2N^+ + e^- \rightarrow HC_5N + H$

Or an indirect relation: example of CO
the most "important" reaction using sensitivity analysis: $C + H_2 \rightarrow CH_2$

Strategy

0D gas-phase model + absorption/desorption processes

Fixed parameters:
$\zeta = 1.3 \times 10^{-17} s^{-1}$, low metal elemental abundances, Av=10

Different models:
1) 10K, $2 \times 10^4 cm^{-3}$, all initial C into C+
2) 10K, $2 \times 10^4 cm^{-3}$, half initial C into CO
3) 10K, $2 \times 10^5 cm^{-3}$, all initial C into C+
4) 10K, $2 \times 10^5 cm^{-3}$, half initial C into CO

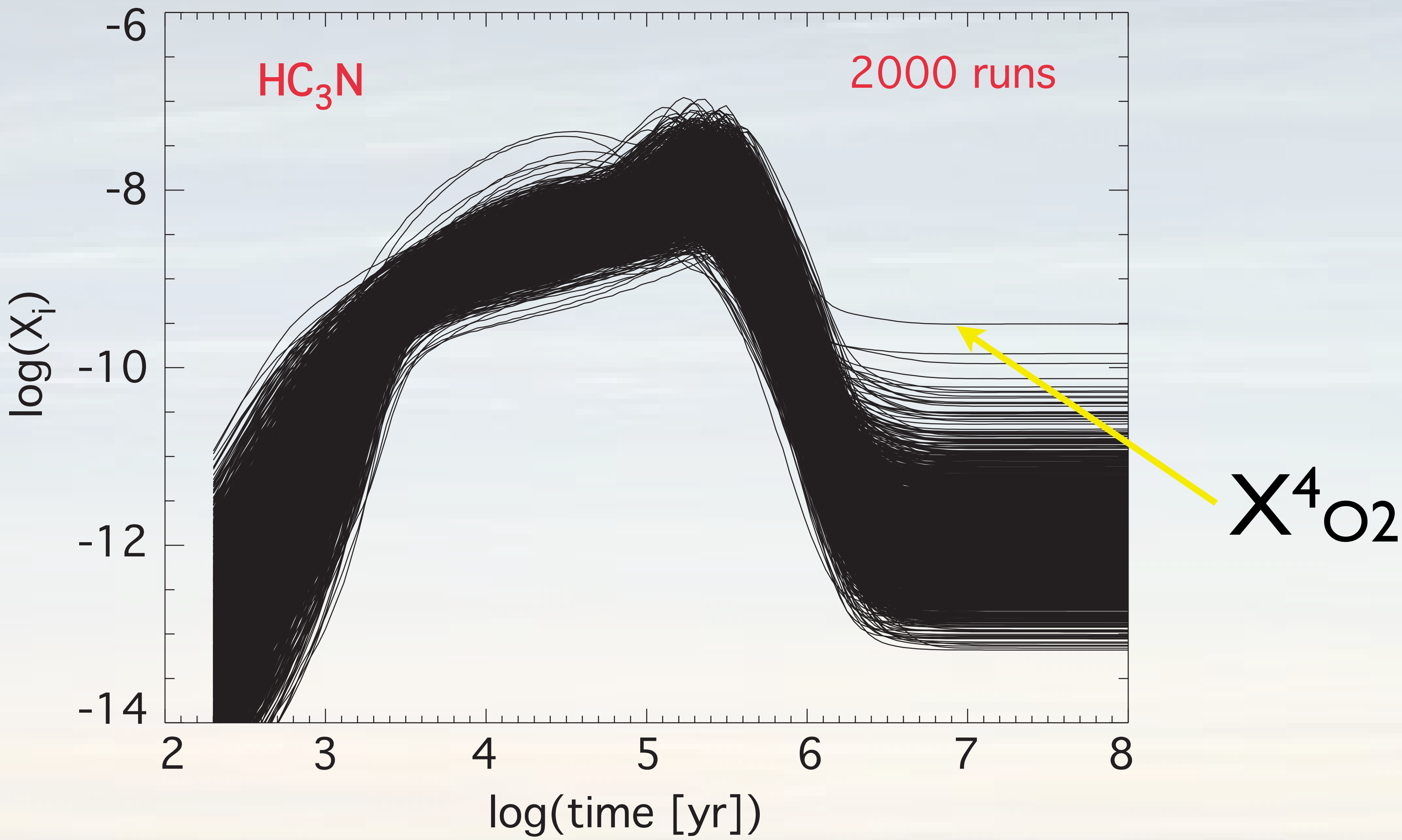
Amount of variation:
1) f=uncertainty range (~x2)
2) f=factor of 10 for all reactions

8 models x 2500 runs

Method:
random variation of the rate coefficients between k/f and k x f.
Computation of Pearson correlation coefficients.

Criteria for the selection of important reactions:
Consider only abundant species ($x > 10^{-11}$)
Two times: 10^5 and 10^6 yr
Correlation coefficients larger than 0.3

Pearson correlation coefficients



$$P_j^i(t) = \frac{\sum^l (X_j^l - \bar{X}_j)(k_i^l - \bar{k_i})}{\sqrt{(\sum^l (X_j^l - \bar{X}_j)^2 \sum^l (k_i^l - \bar{k_i})^2}}$$

X abundance species, $\overline{X}$ mean abundance
k rate coefficient, $\overline{k}$ mean rate coefficient

Results

Table 1: List of reactions that influence several species

Reaction	Concerned species
$C + H_2 \rightarrow CH_2$ + photon	73
$CH_3^+ + H_2 \rightarrow CH_5^+$ + photon	18
$C_2H_2^+ + H_2 \rightarrow C_2H_4^+$ + photon	C_2H_2O; C_2H_3, $C_2H_2^+$, C_2HO^+, $C_2H_2N^+$, $C_2H_4^+$
$CH_3^+ + CO \rightarrow C_2H_3O^+$ + photon	C_2H_2O, $C_2H_3O^+$
$C_2H_4^+ + e^- \rightarrow C_2H_3 + H$	C_2H_2O, C_2H_3
$HSiO^+ + e^- \rightarrow SiO + H$ **$HSiO^+ + e^- \rightarrow Si + OH$**	Si, SiO
$C_3H+ + H_2 \rightarrow C_3H_3^+$ + photon $C_3H+ + H_2 \rightarrow H_3C_3^+$ + photon	C_3H_2, H_2C_3, C_3H^+, $C_3H_2^+$, $C_3H_3^+$, $H_3C_3^+$
$CH_3^+ + HCN \rightarrow C_2H_4N^+$ + photon	C_2H_2N, HC_3N, C_2H_3N, $C_2H_4N^+$
$C_4H_2^+ + H \rightarrow C_4H_3^+$ + photon	C_4H_2, C_5H, C_6H_6, $C_4H_3^+$
$CH_3^+ + NH_3 \rightarrow CH_6N^+$ + photon	CH_3N, CH_5N
$C_4H_2^+ + O \rightarrow HC_4O^+ + H$	C_3O, HC_4O^+

Results

Table 2: List of reactions for abundant and observed species

Reaction	Concerned species
Neutral-Neutral reactions	
$C + C_3O \rightarrow C_3 + CO$	C_3O
$C + OCN \rightarrow CO + CN$	OCS
$H + CH_2 \rightarrow CH + H_2$	CH
$O + CN \rightarrow CO + H$	CN
$N + CN \rightarrow C + N_2$	CN
$O + NH \rightarrow NO + H$	NH
$O + C_2 \rightarrow CO + C$	C_2
$O + C_2H \rightarrow CO + CH$	C_2H
$O + C_3H \rightarrow C_2H + CO$	C_3H
$N + C_3 \rightarrow CN + C_2$	C_3
$N + NO \rightarrow N_2 + O$	NO
$O + NH_2 \rightarrow HNO + H$	NH_2
$O + HNO \rightarrow NO_2 + H$ $O + HNO \rightarrow N_2O + H$	N_2O
$CN + NH_3 \rightarrow NH_2CN + H$	NH_2CN
$O + C_3N \rightarrow CO + C_2N$	C_3N
$N + C_4N \rightarrow CN + C_3N$	C_4N
$N + C_4H \rightarrow C_4N + H$	C_4N
$N + C_2N \rightarrow CN + CN$	C_2N
$CN + HC_5N \rightarrow NC_6N + H$	NC_6N
$CN + HC_3N \rightarrow NC_4N + H$	NC_4N

Association reactions	
$C_4H_2^+ + HC_3N \rightarrow C_7H_3N^+$ + photon	HC_7N
HS+ + $H_2 \rightarrow H_3S^+$ + photon	H_2S
$HCO^+ + H_2O \rightarrow CH_3O_2^+$ + photon	CH_2O_2
$C^+ + H_2 \rightarrow CH_2^+$ + photon	C_3
S + CO → OCS + photon	OCS
$CH_3^+ + HC_3N \rightarrow C_4H_4N^+$ + photon	CH_3C_3N
$CH_3^+ + HC_5N \rightarrow C_6H_4N^+$ + photon	CH_3C_5N
$Si^+ + H_2 \rightarrow SiH_2^+$ + photon	HNSi

Ion-neutral reactions	
$C_2H_3^+ + O \rightarrow C_2H_2O^+ + H$	$C_2H_2O^+$
$C^+ + S \rightarrow S^+ + C$	H_2CS
$C_5H^+ + N \rightarrow C_5N^+ + H$	$C_5H_2N^+$, HC_5N
$C_2H_4^+ + N \rightarrow C_2H_2N^+ + H_2$	$C_2H_2N^+$
$C_4H_2^+ + S \rightarrow HC_4S^+ + H$	C_4S
$H_3^+ + C \rightarrow CH^+ + H_2$	C_3H_3
$H_3^+ + O \rightarrow OH^+ + H_2$	H_3O^+
$C_2H_3^+ + N \rightarrow C_2NH^+$ + H2	C_2NH^+

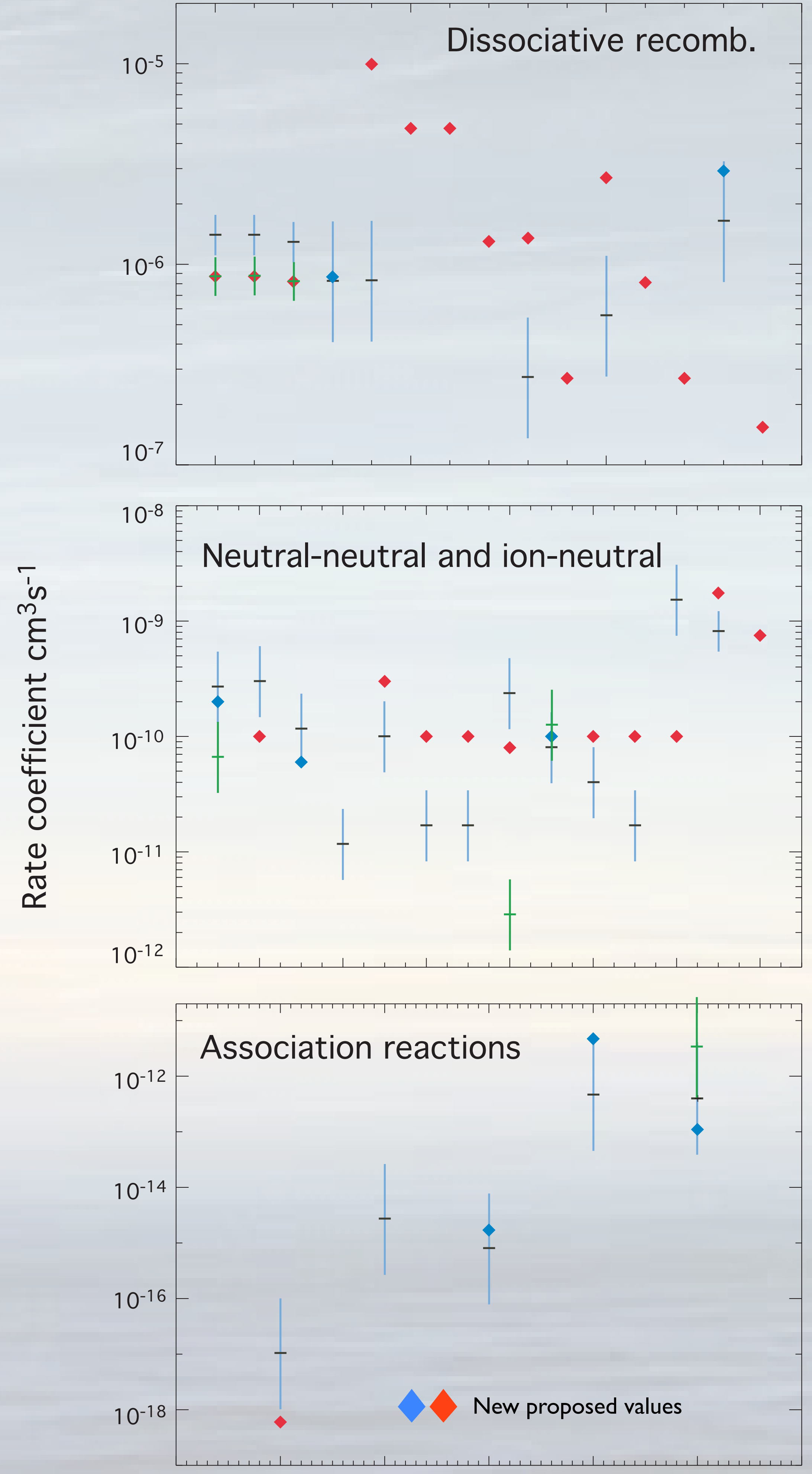
Dissociative recombination	
$HC_4O+ + e^- \rightarrow C_3O + CH$	C_3O
$H_2NC^+ + e^- \rightarrow HNC + H$	HNC, H_2NC^+
$C_5H_2N^+ + e^- \rightarrow C_5N + H_2$	$C_5H_2N^+$
$HC_4S^+ + e^- \rightarrow C_4S + H$	C_4S
$H_2CO^+ + e^- \rightarrow CO + H + H$	H_2CO^+
$CNC^+ + e_- \rightarrow CN + C$	CNC^+
$HC_4S^+ + e^- \rightarrow C_4S + H$	C_4S
$HC_3S^+ + e^- \rightarrow C_3S + H$ $HC_3S^+ + e^- \rightarrow C_2S + CH$	C_3S

Impact of the new rate coefficients on the model predictions

V. Wakelam

Proposed modifications

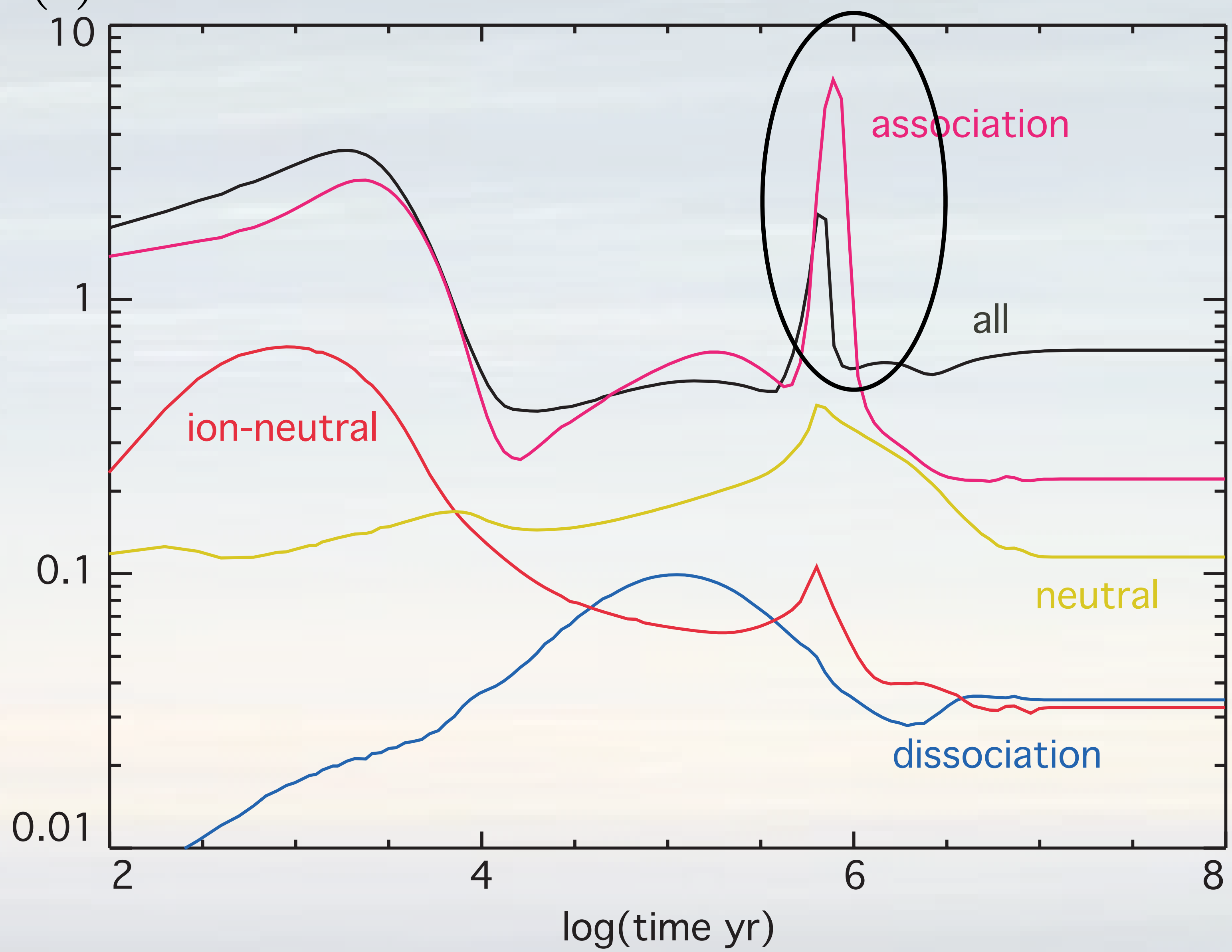
34 reactions studied in total
Proposed changes:
11/18 neutral-neutral
2/2 ion-neutral
5/5 association reactions
4/9 dissociative recombination



Comparison with the OSU rate coefficients at 10K

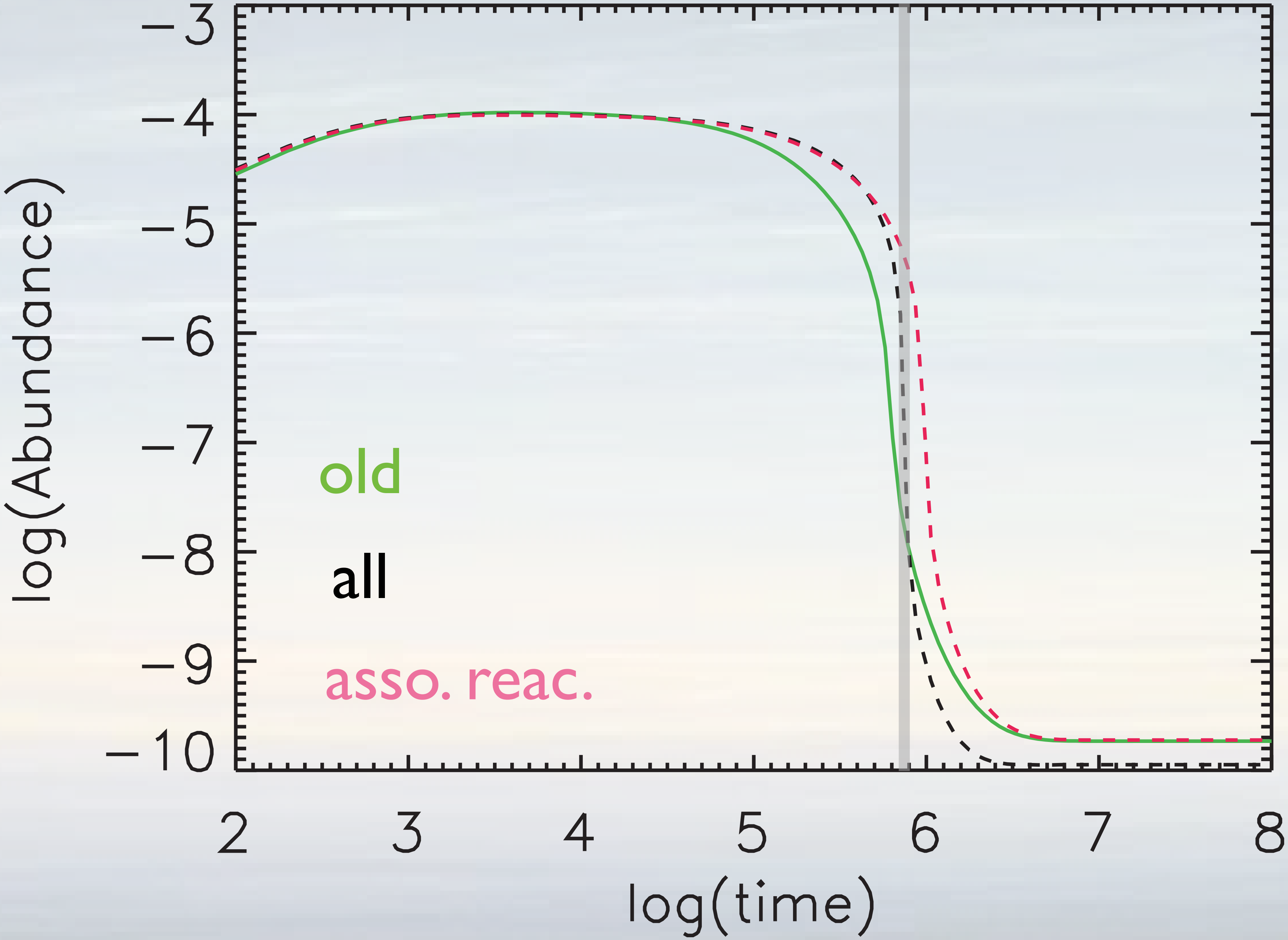
General impact of the new rate coefficients

$$\frac{1}{n_j} \sum_j \left| \frac{(X_j^i(t) - X_j^{ref}(t))}{X_j^{ref}(t)} \right|$$

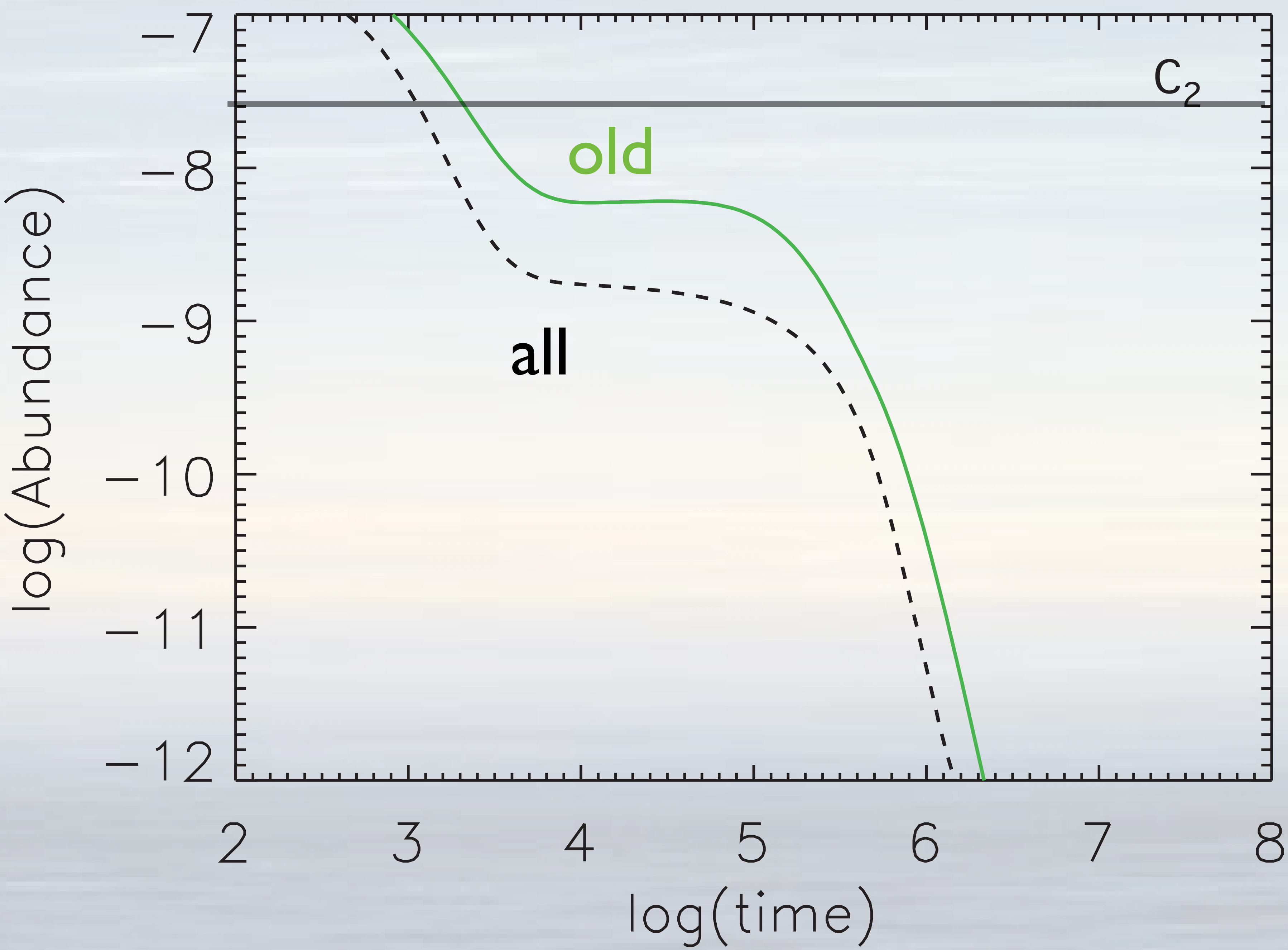


The identified association reactions impact more species.

Atomic carbon

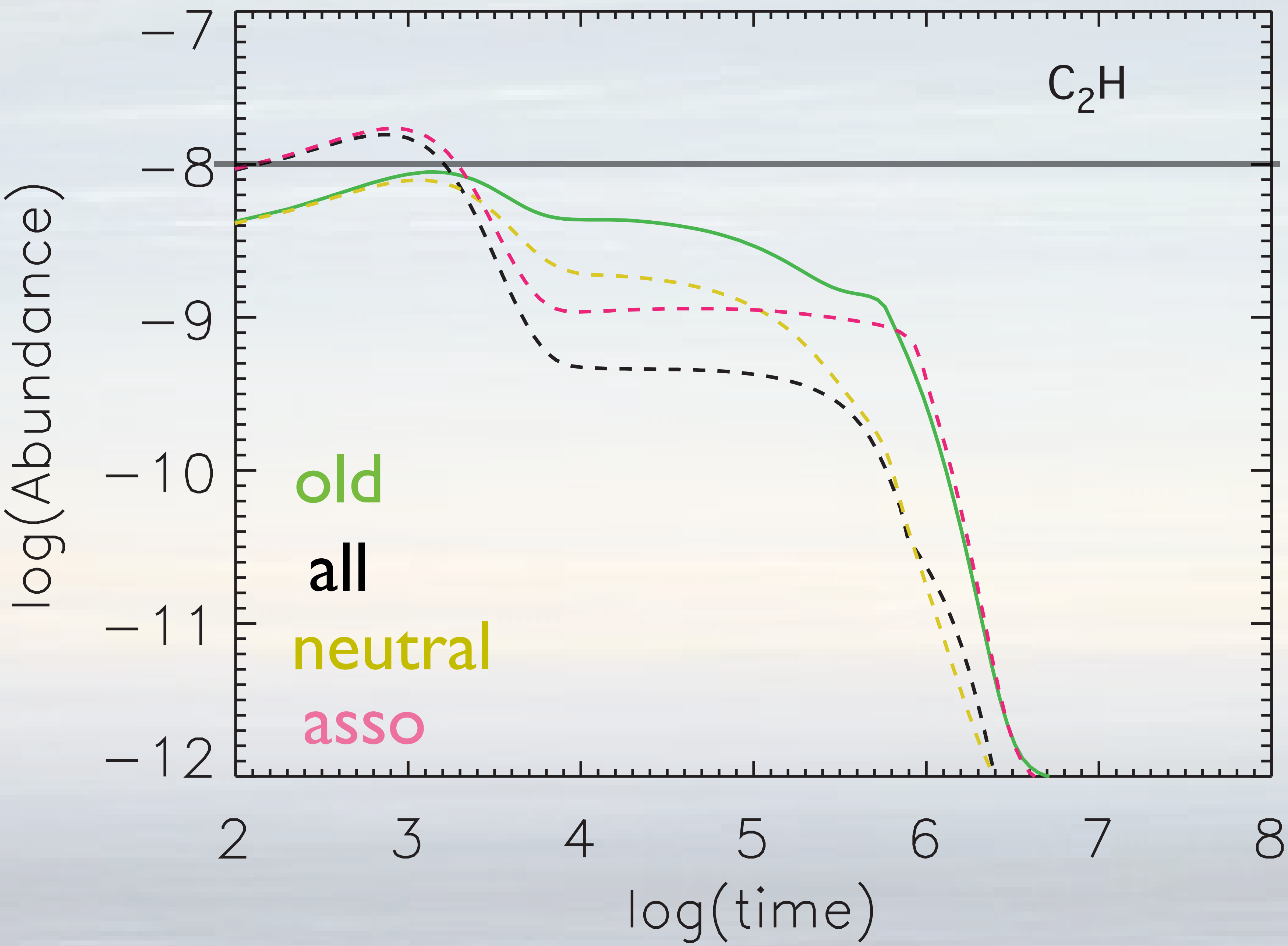


Reaction O + C_2 → CO + C increased by a factor 3

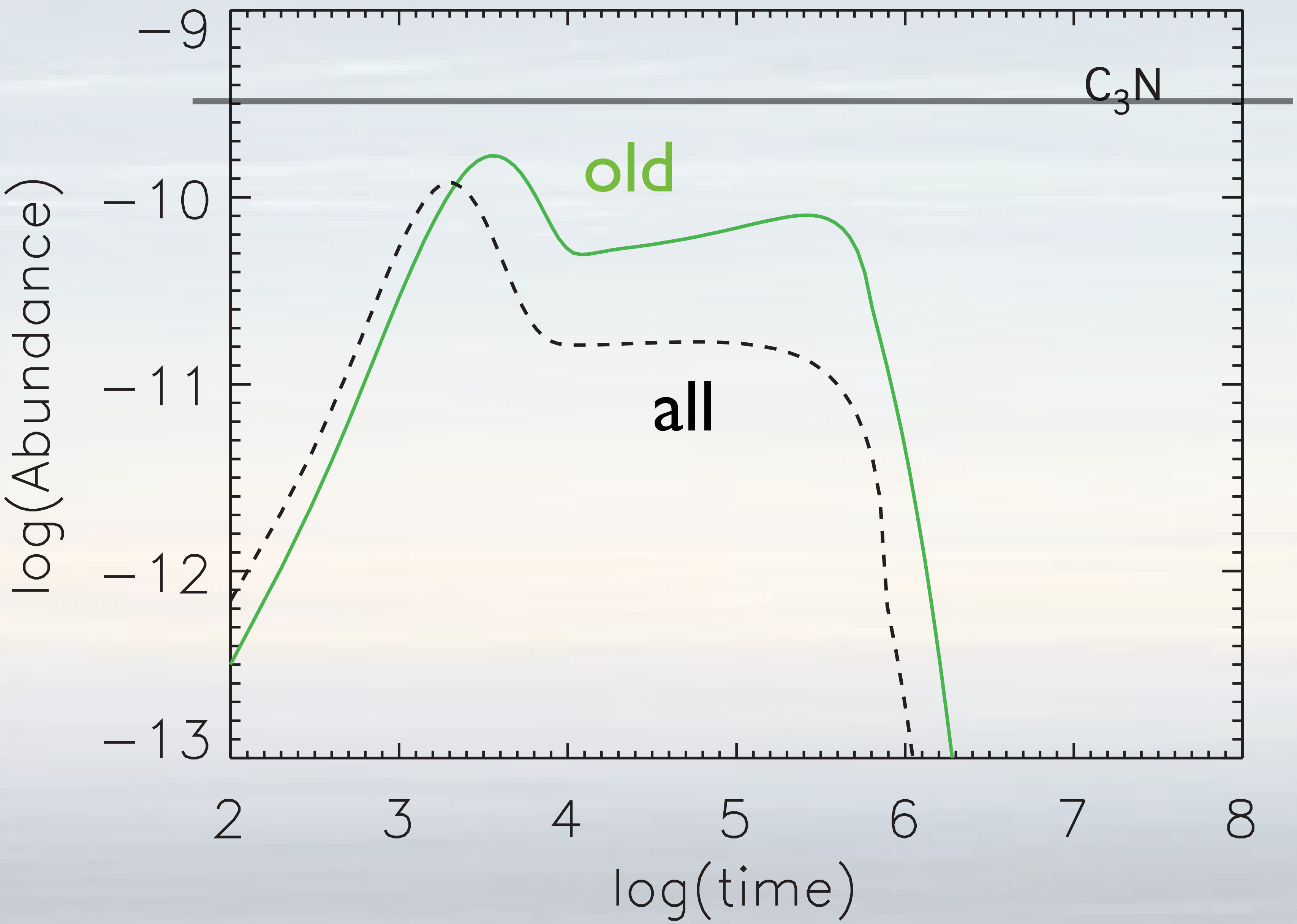


Reaction O + C_2H → CO + CH decreased by a factor of 10

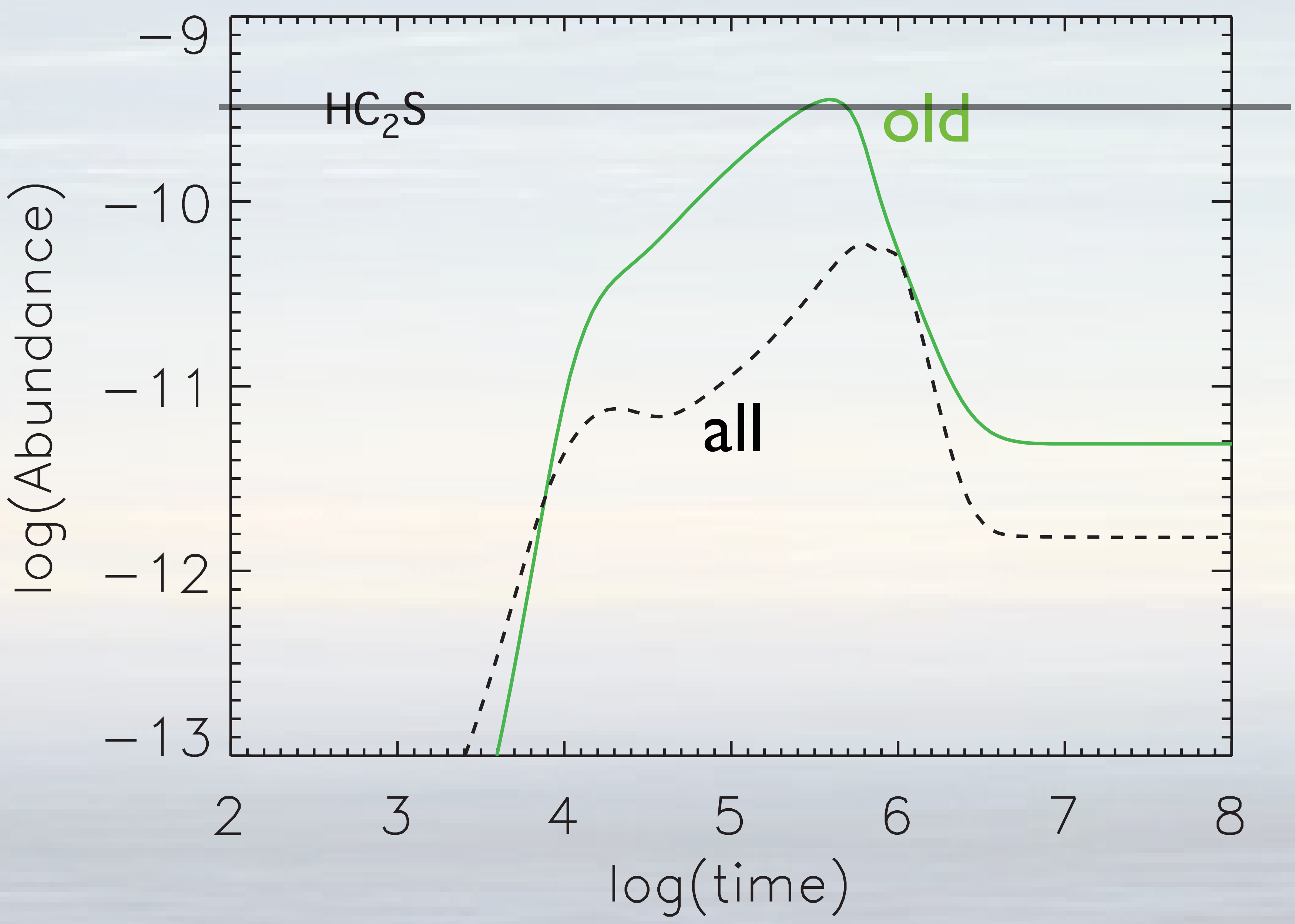
Reaction C + H_2 → CH_2 decreased by more than a factor of 10



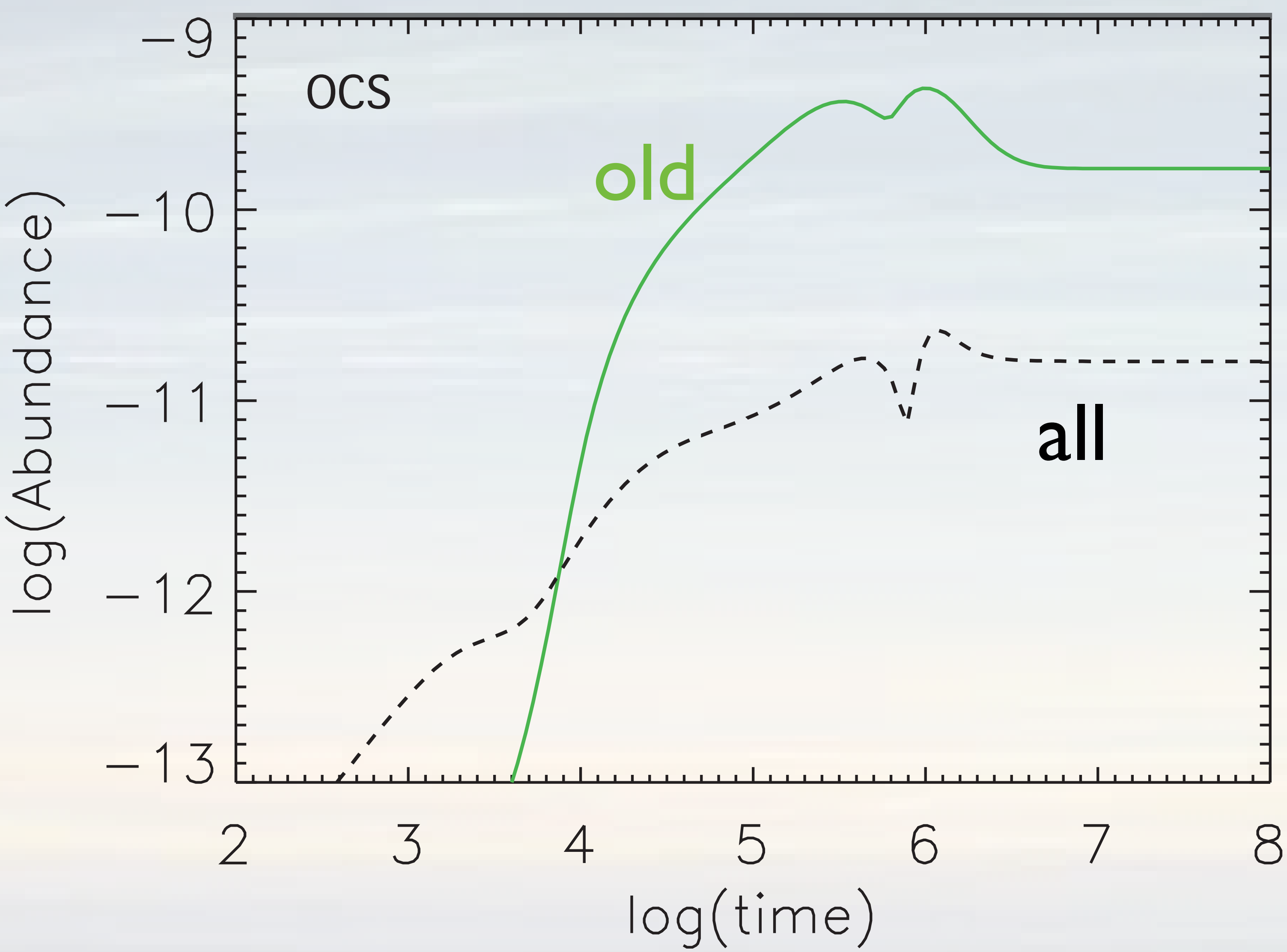
Reaction O + C_3N → CO + C_2N decreased by about a factor of 2 + combined effect with other reactions...



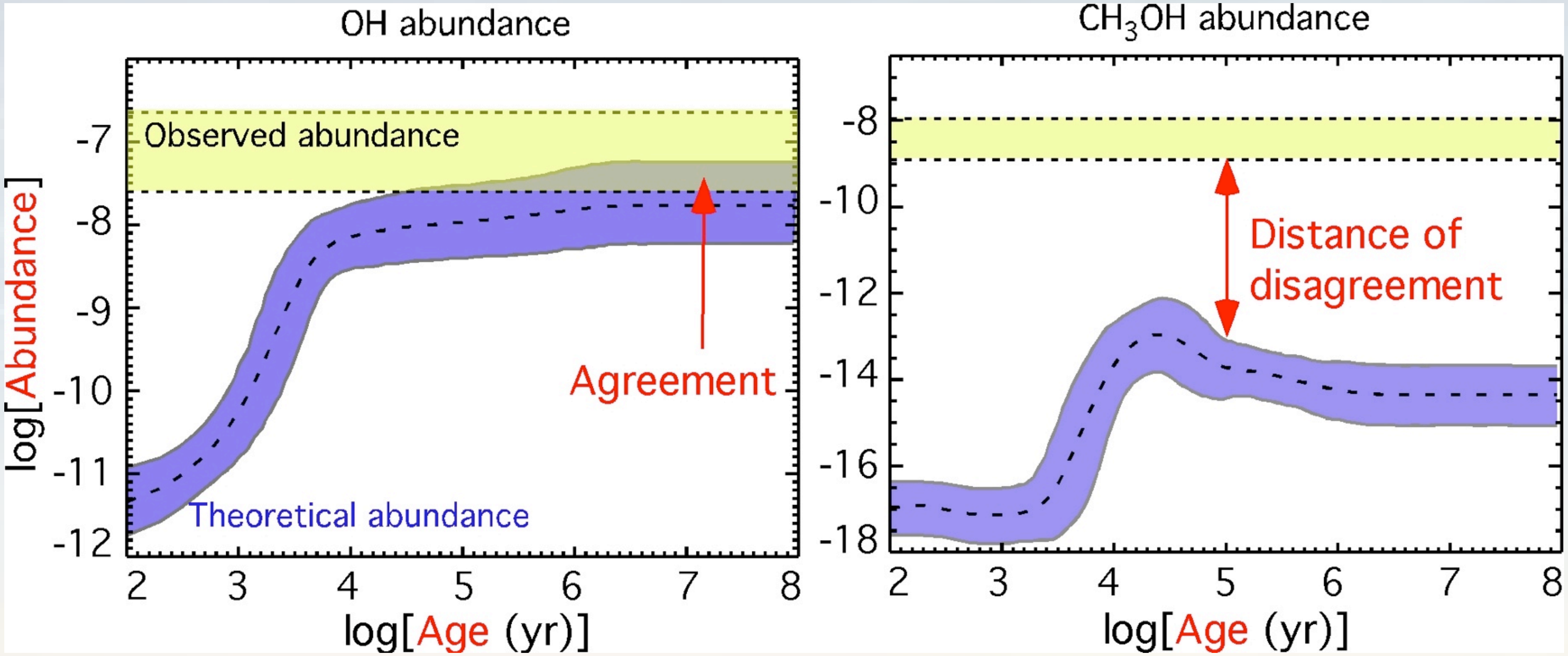
Reaction $C^+ + S \rightarrow C + S^+$ decreased by about a factor of 10 + combined effect with $C + H_2 \rightarrow CH_2$



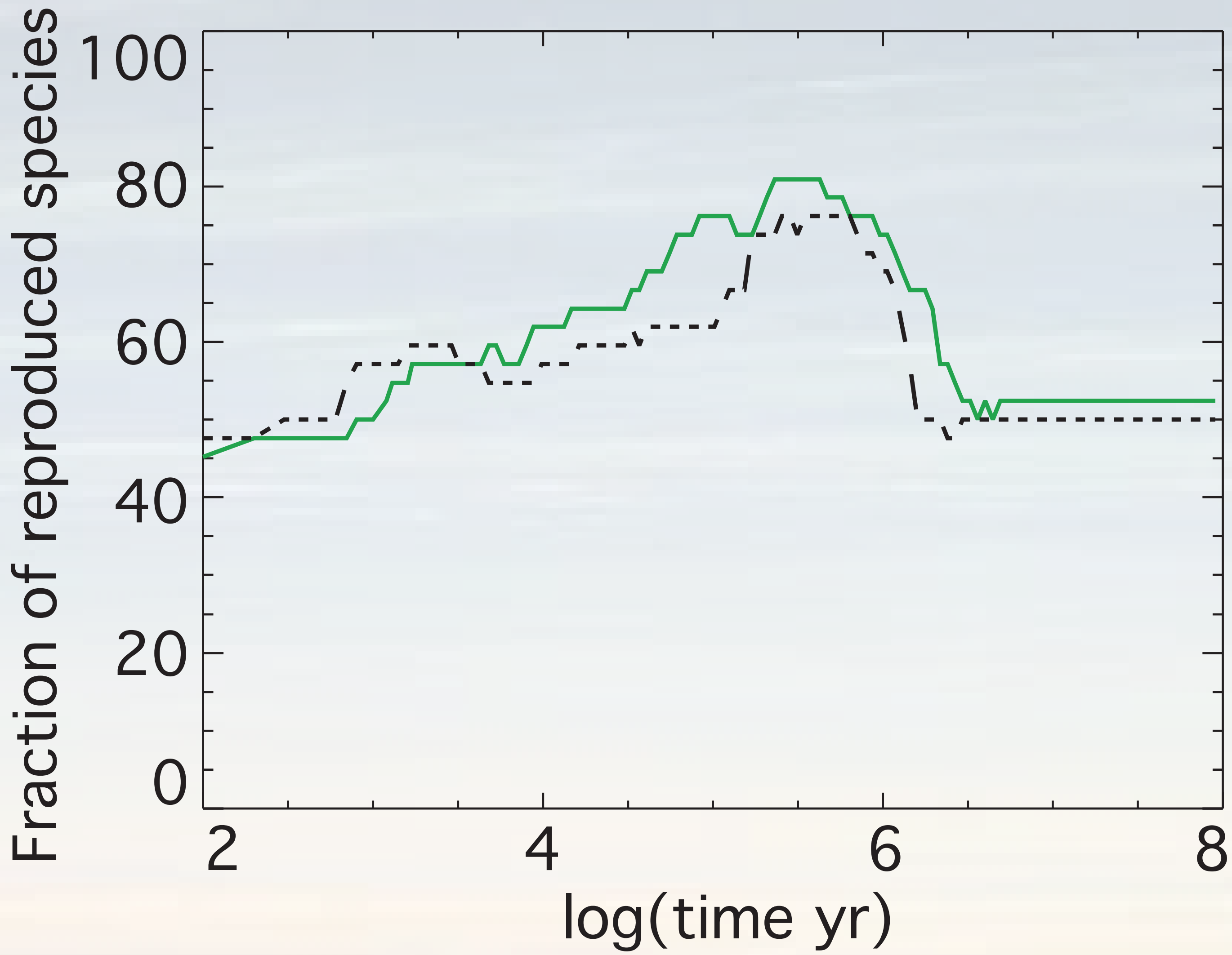
Reaction CS + O → OCS set to 0



Comparison between models and observations



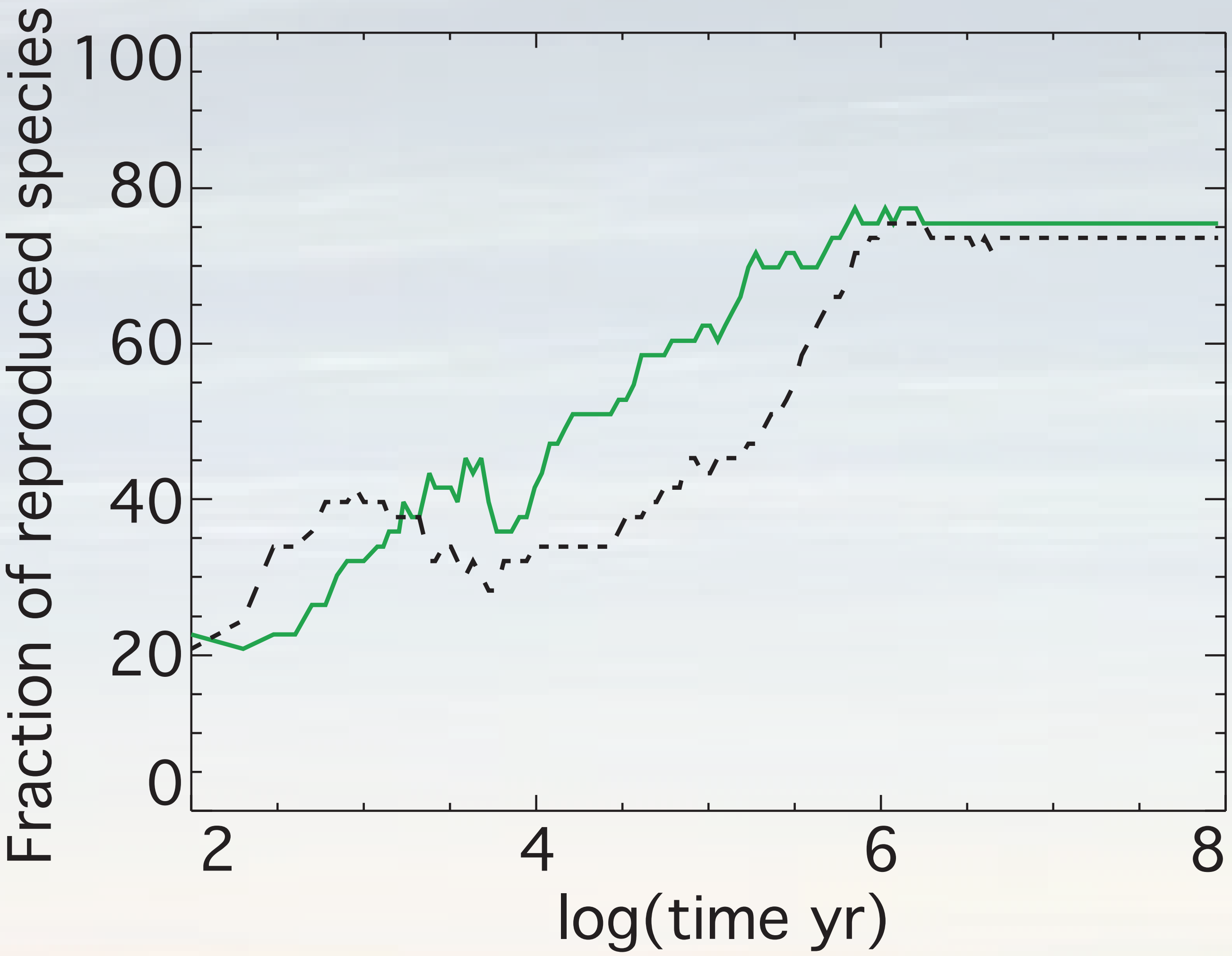
Molecular cloud: L134N (42 observed species)



Old rate coefficients:
80.9% of observed abundances reproduced by the model
non-reproduced molecules: NO, H_2S, CH_3OH, CH_3CHO, HC_7N, HCO^+, HCS^+ and SiO

New rate coefficients:
76.2% of observed abundances reproduced by the model
non-reproduced molecules: CH, H_2S, OCS, CH_3OH, CH_3CHO, HC_5N, HC_7N, HCO^+, HCS^+ and SiO

Molecular cloud: TMC1 (53 observed species)



Old rate coefficients:
77% of observed abundances reproduced by the model
non-reproduced molecules: CN, OH, CH_3OH, CH_3CHO, C_3H_3N, C_3H_4, CH_3C_3N, HC_9N, HCO^+, HCS^+, H_2NC^+ and SiO

New rate coefficients:
75% of observed abundances reproduced by the model
non-reproduced molecules: CN, OH, C_2H, OCS, CH_3OH, CH_3CHO, C_3H_3N, C_3H_4, CH_3C_3N, HC_5N, HC_9N, HCO^+, HCS^+, H_2NC^+ and SiO

Summary

34 reactions were studied and 65% were changed.

Association reactions have an impact on many reactions.
Other reactions can have an impact on specific species.
Non linear effects have been seen (combined effects of modified reactions).

The modifications worsen the agreement with observations: OCS and HC_5N.