Modeling the formation of interstellar CO_2, CO and water ice

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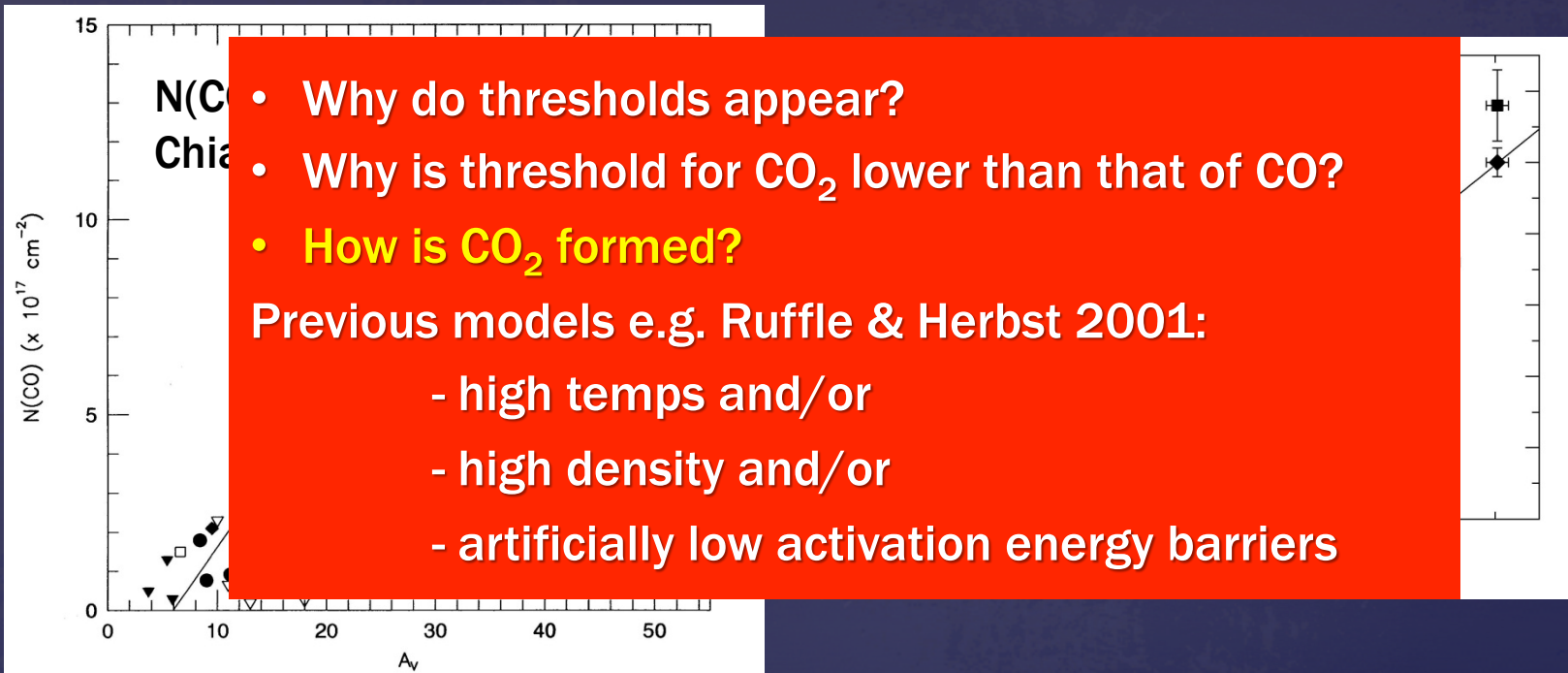(My NSF REU student at Cornell, summer 2010)

Cornell University

Interstellar H_2O, CO_2, CO ices

- Ices form on dust-grain surfaces

- Ices detected through IR absorption band spectroscopy

- Taurus dark cloud is best-defined example (Whittet & co.)

- Shape of spectra $\Rightarrow$ Most CO_2 is in polar mixture (i.e water-rich)

- Smaller component in apolar mixture with CO

- CO_2 formation chemistry is a problem (for theoreticians)
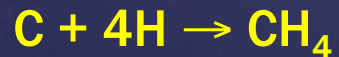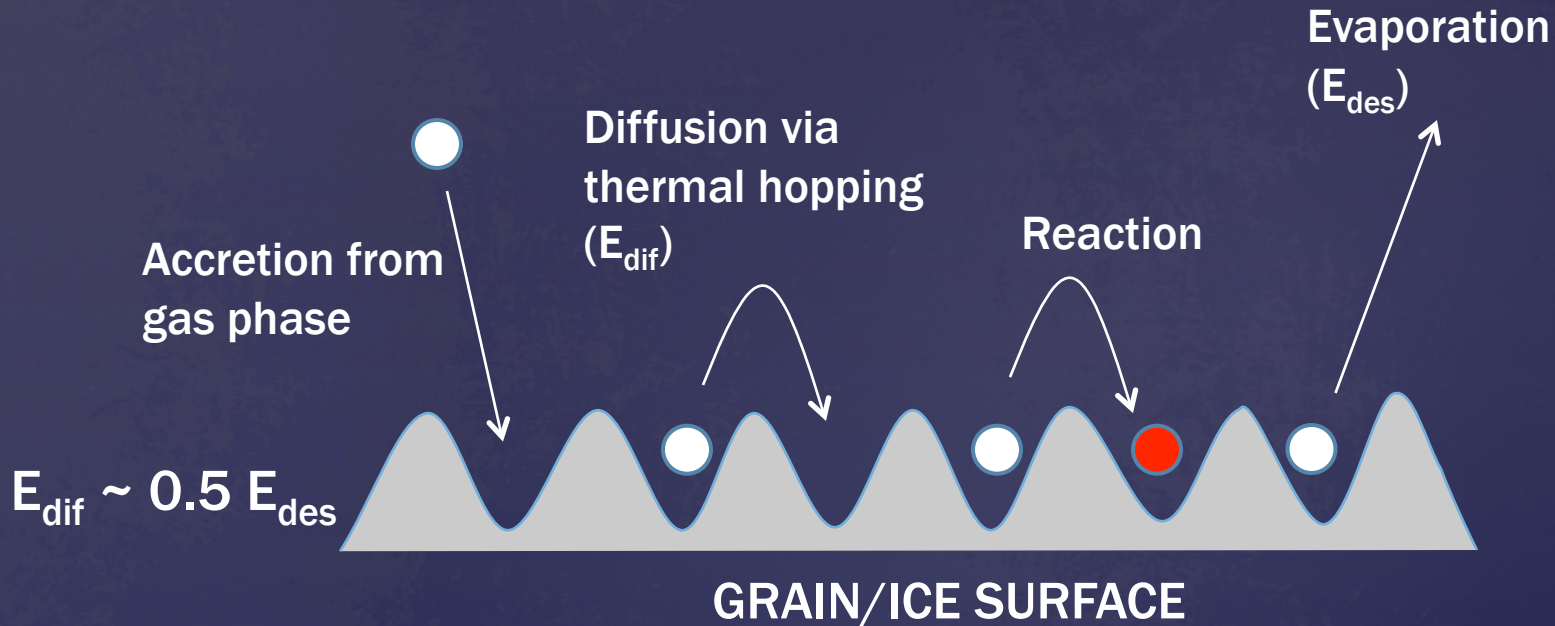
Extinction thresholds (Taurus dark cloud)

N(CO...
Chia...

N(CO) ($\times 10^{17}$ cm^{-2})

A_V

- **Why do thresholds appear?**
- **Why is threshold for CO_2 lower than that of CO?**
- **How is CO_2 formed?**

Previous models e.g. Ruffle & Herbst 2001:

    - high temps and/or

    - high density and/or

    - artificially low activation energy barriers

$A_{V,th}(H_2O) = 3.2 \pm 0.1$

$A_{V,th}(CO_2) = 4.3 \pm 1.0$

$A_{V,th}(CO) = 6.7 \pm 1.6$

(All Whittet+ 2007)

Surface chemistry processes

Evaporation (E_{des})

Diffusion via thermal hopping (E_{dif})

Reaction

Accretion from gas phase

$E_{dif} \sim 0.5\ E_{des}$

GRAIN/ICE SURFACE

$O + 2H \rightarrow H_2O$
$C + 4H \rightarrow CH_4$

CO formed in <u>gas phase</u>, then accretes

$CO + 4H \rightarrow CH_3OH$ (act. Barriers)

CO_2 chemistry

- **Three grain-surface reactions usually considered:**

  (1) $CO + O \rightarrow CO_2$ $\kappa_{tunnel} = 4.8 \times 10^{-23}$

    (Goumans & Andersson 2010)

  (2) $HCO + O \rightarrow CO_2 + H$ (no barrier)

  (3) $CO + OH \rightarrow CO_2 + H$ $E_A = 80\ K\ ?$

- **Reaction (3) could also happen like this:**

  $H + O + \underline{CO} \rightarrow OH + \underline{CO} \rightarrow CO_2 + H$

    (now added to the chemical network)

More CO_2 chemistry:
$CO + OH \rightarrow CO_2 + H$ (i.e. reaction 3)

- $CO + OH \rightarrow HOCO^*$
  - Small or even negative barrier

    (Song+ 2006; Chen & Marcus 2005)

- Once through initial barrier, either:
  - (i) $HOCO^* \rightarrow CO + OH$
  - (ii) $HOCO^* \rightarrow CO_2 + H$
  - (iii) $HOCO^* + surf. \rightarrow HOCO + surf.$
    - then $HOCO + H \rightarrow CO_2 + H$

    Other products? (Goumans+ 2008)

- Oba et al. 2010: Surface experiments with CO + OH reaction
  - $\rightarrow CO_2$ is formed, no alternative products.
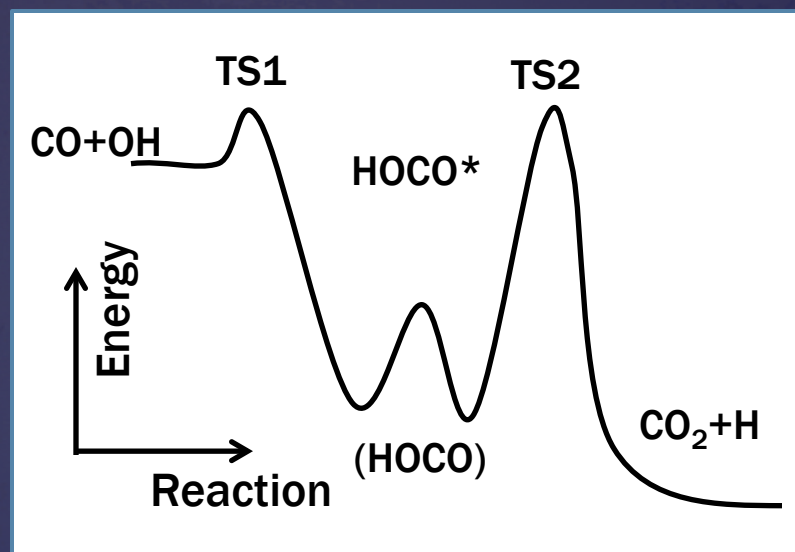
CO + OH efficiency and competition

- If small initial barrier is overcome, reaction probably $\rightarrow$ CO_2

- If (simplistically):

  [activation barrier] << [diffusion barrier of CO]

...then OH + CO $\rightarrow$ CO_2 + H goes with efficiency ~100
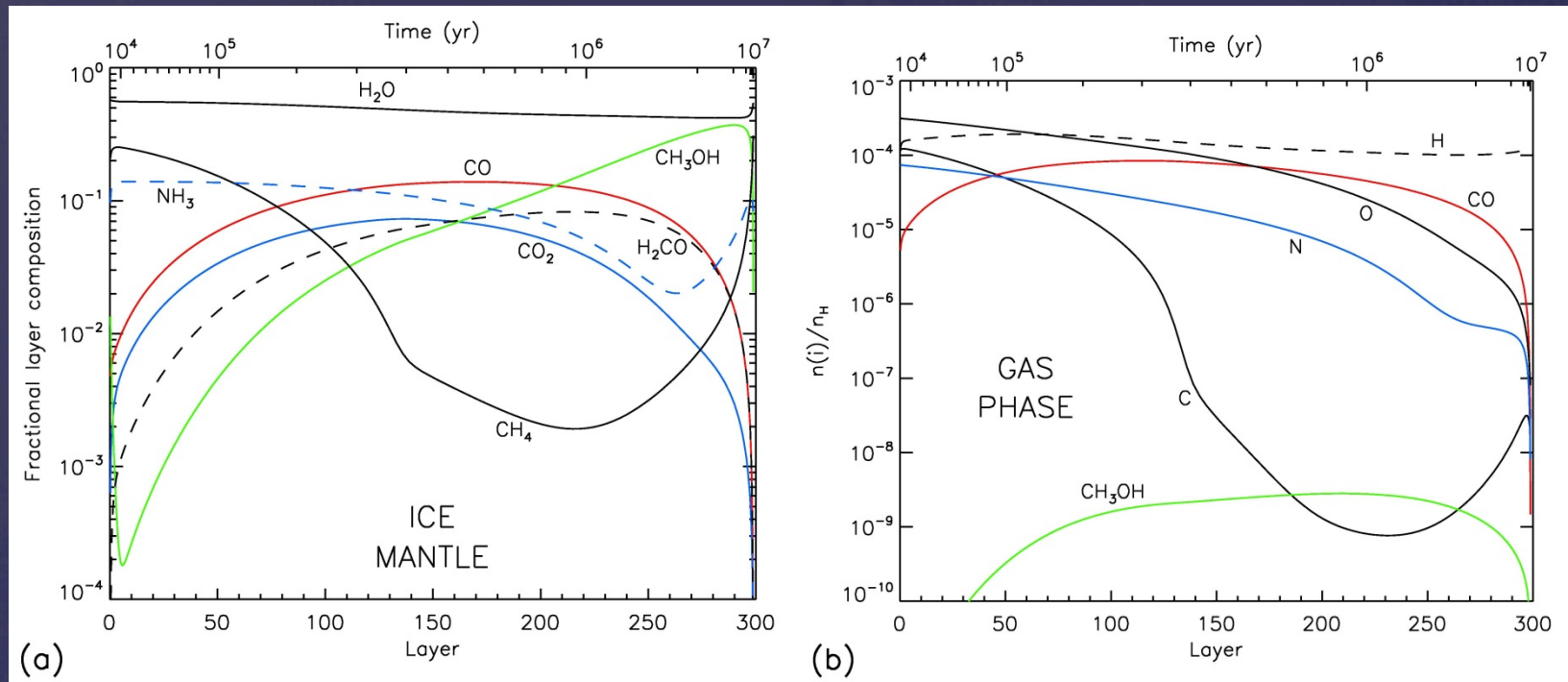
  (Not the same as gas-phase reactions)

- This has been ignored in previous models!

- So, we stick with E_A = 80 K barrier $\Rightarrow$ efficiency ~100%

New chemical model
(Garrod & Pauly, submitted)

- 3-phase: Gas phase / Surface / Mantle
                       (after Hasegawa & Herbst 1993)

- Allows chemical composition of each layer to be traced (and preserved)

- Treats chemistry as a surface phenomenon (true for low temps)

- Competition between barrier-mediated reactions and diffusion
        (previous gas-grain models have not treated this properly!)

- Chemical network of Garrod et al. (2008)

- Rate equations (modified rates as per Garrod 2008)

- Reactive desorption (Garrod et al. 2007) and photodesorption (Öberg et al. 2009)

Grain-mantle composition by layer:

(a) ICE MANTLE — Fractional layer composition vs Layer / Time (yr)

(b) GAS PHASE — $n(i)/n_H$ vs Layer / Time (yr)

DARK CLOUD:

$n_H = 2 \times 10^4$ cm^{-3}

$A_V = 10$

$T_{gas} = T_{dust} = 10$ K

$E_{dif} = 0.5\ E_{des}$

- CO is good: ~20 % w.r.t. water ice
- CO_2 is good: $CO/CO_2 = 2 - 4$
  (cf. Bergin+ 2005: 100:26 toward Elias 16)
- Methanol associated w/ oxygen depletion
- No early CO_2, and CO_2 never dominates
- **Formation of CO_2 by O+H+CO reaction**

Where does CO_2-dominant phase come in?

(a) T_{dust} = 8 K — ICE MANTLE

(b) T_{dust} = 12 K — ICE MANTLE
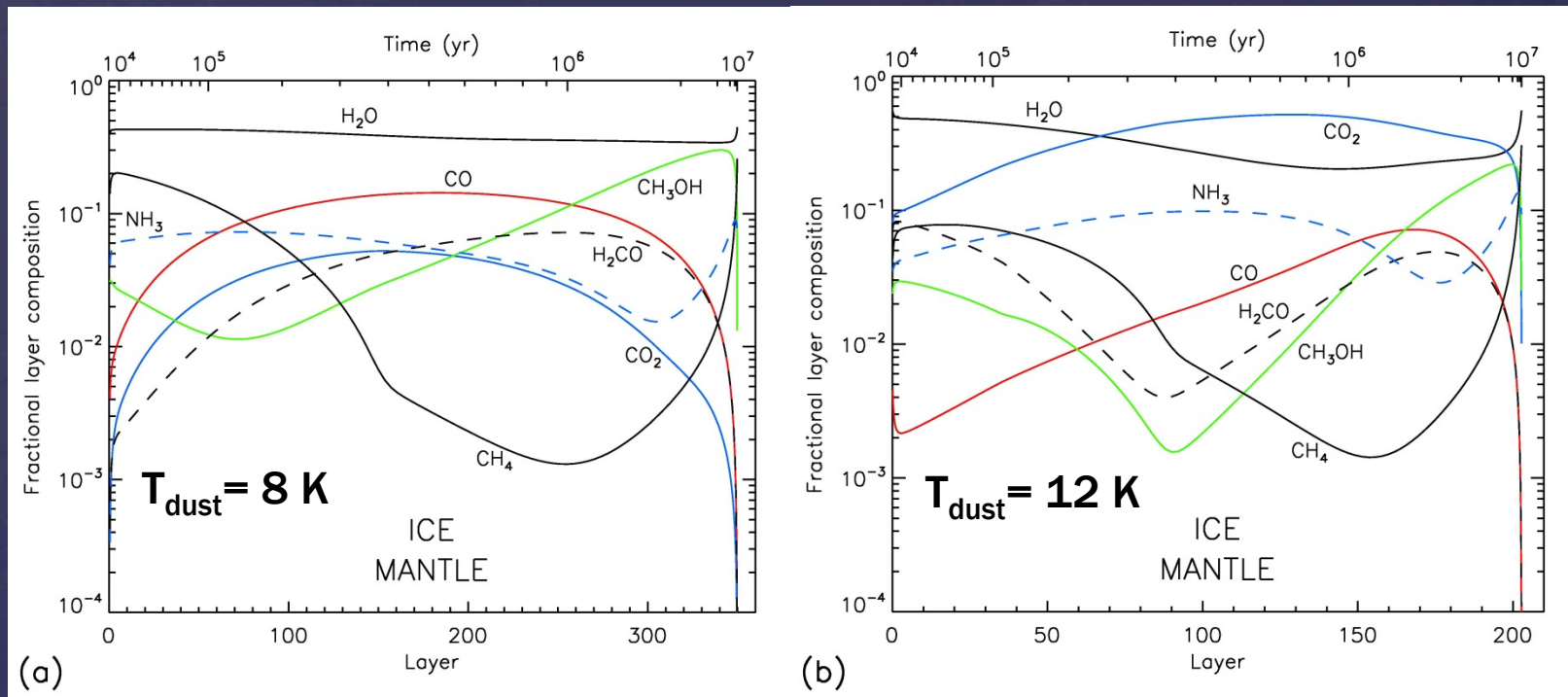
E_{dif} = 0.3 E_{des}

- CO_2:CO behavior is robust up to 12 K
- <12 K: $O + H + CO \rightarrow CO_2 + H$ is dominant
- >12 K: mobile $CO + OH \rightarrow CO_2 + H$
    - polar CO_2

Depth/temp-dependent cloud models

- Interested in effects of dust temperature
- Balance absorption of ISRF with thermal emission of grains
- Radiation field of Zucconi et al. (2001)
- H_2 and CO photodissociation rates of Lee et al. (1998)

- Run model at positions from edge to center of cloud
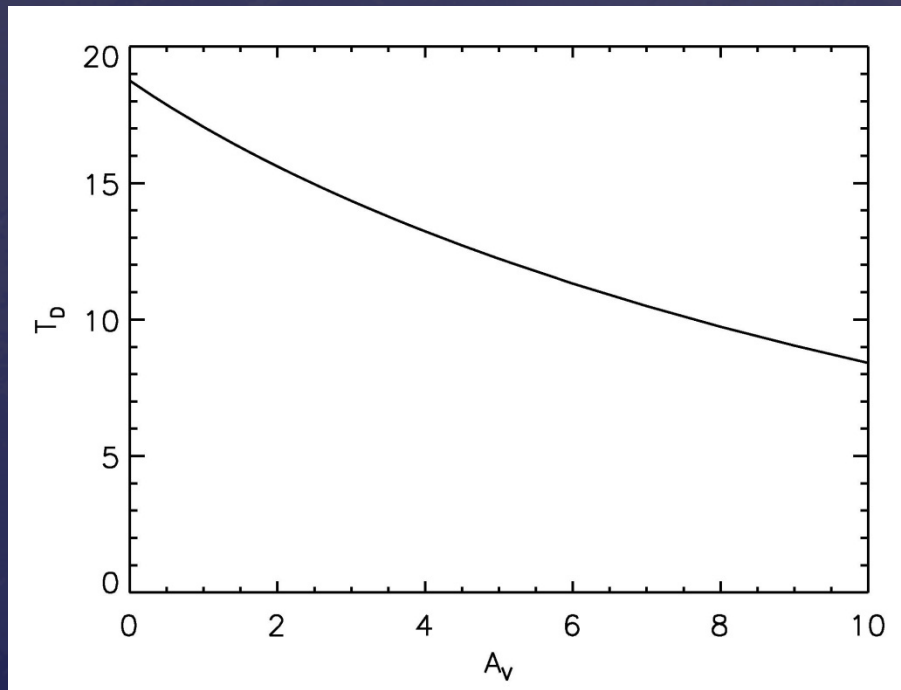
Ice column densities vs. extinction

(a) $n_H = 2\times10^3 \; cm^{-3}$

(b) $n_H = 6\times10^3 \; cm^{-3}$

(c) $n_H = 2\times10^4 \; cm^{-3}$

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(Whittet+ 2007)

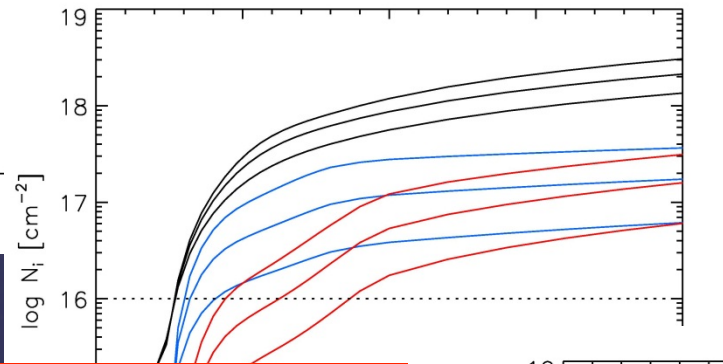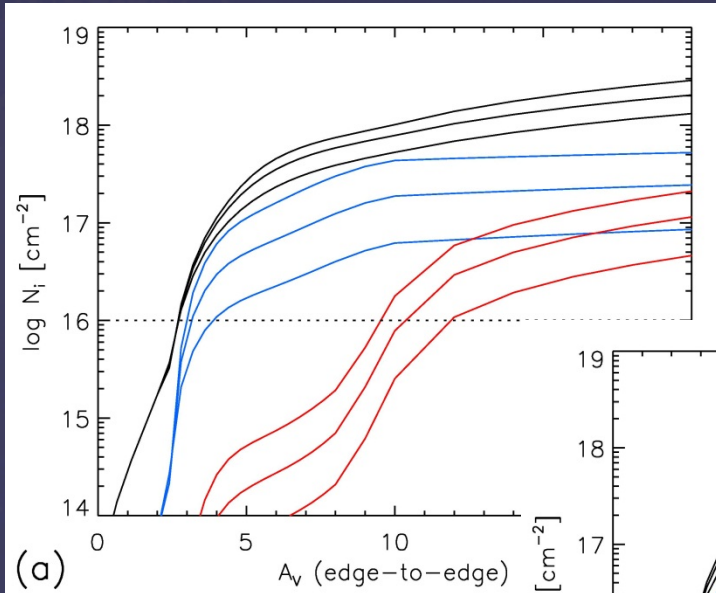Lower curves = 0.5 Myr
Middle curves = 1 Myr
Upper curves = 2 Myr
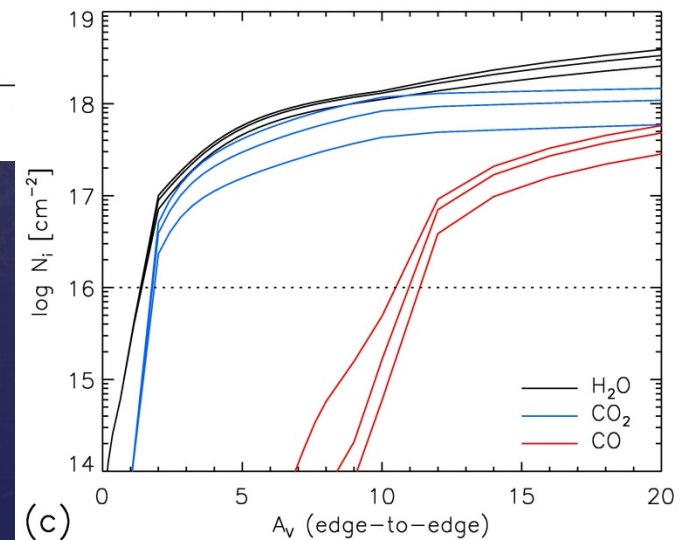
Variation of diffusion barriers

(a) $E_{dif} = 0.35\ E_{des}$

(b) $E_{dif} = 0.4\ E_{des}$

(c) $E_{dif} = 0.45\ E_{des}$

$A_{V,th}(H_2O) = 3.2\pm0.1$

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(Whittet+ 2007)

Model $A_{V,th}$:

$H_2O \sim 3$

$CO_2 \sim 3 - 4$

$CO \sim 4 - 8$

Collapse models

Polar CO$_2$ formed fine

Later CO:CO$_2$ is good
                - but there is still lots of water!
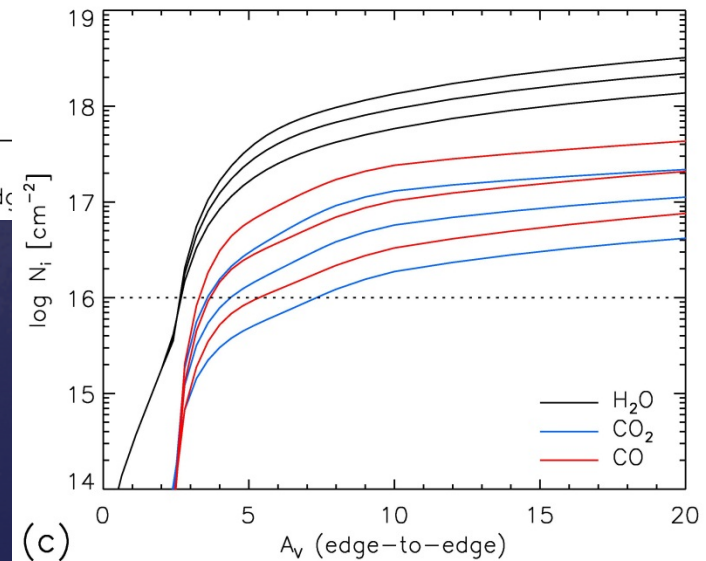
...Maybe H$_2$O and CO/CO$_2$ ices are segregated
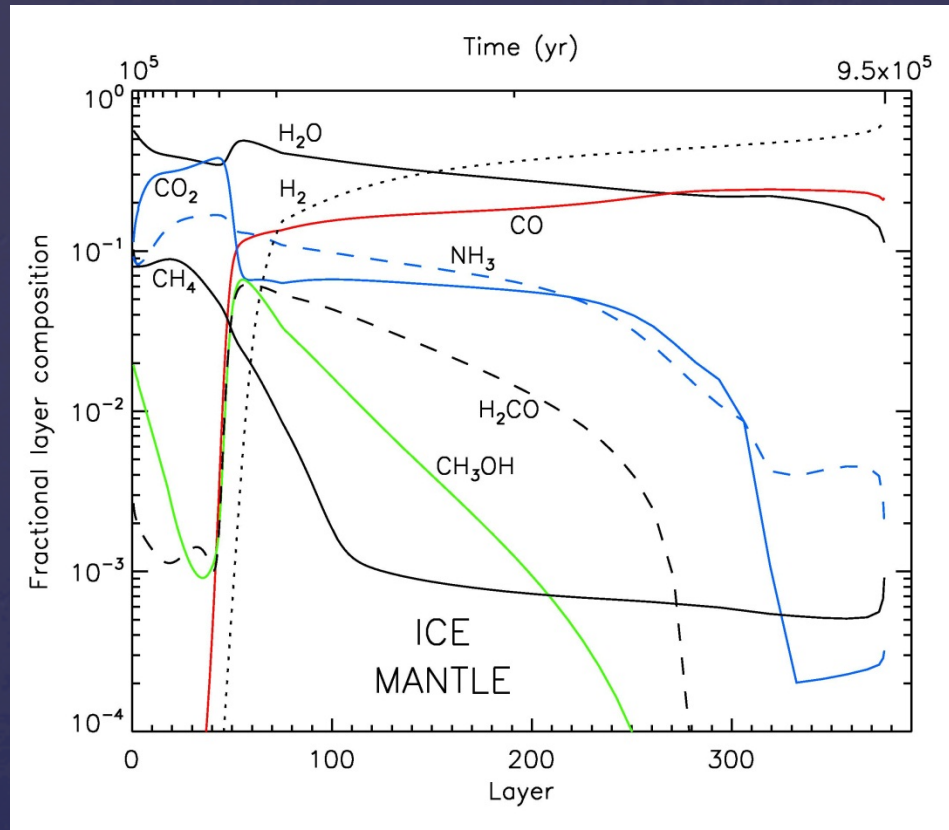   **- diffusion of CO is fast enough for this**
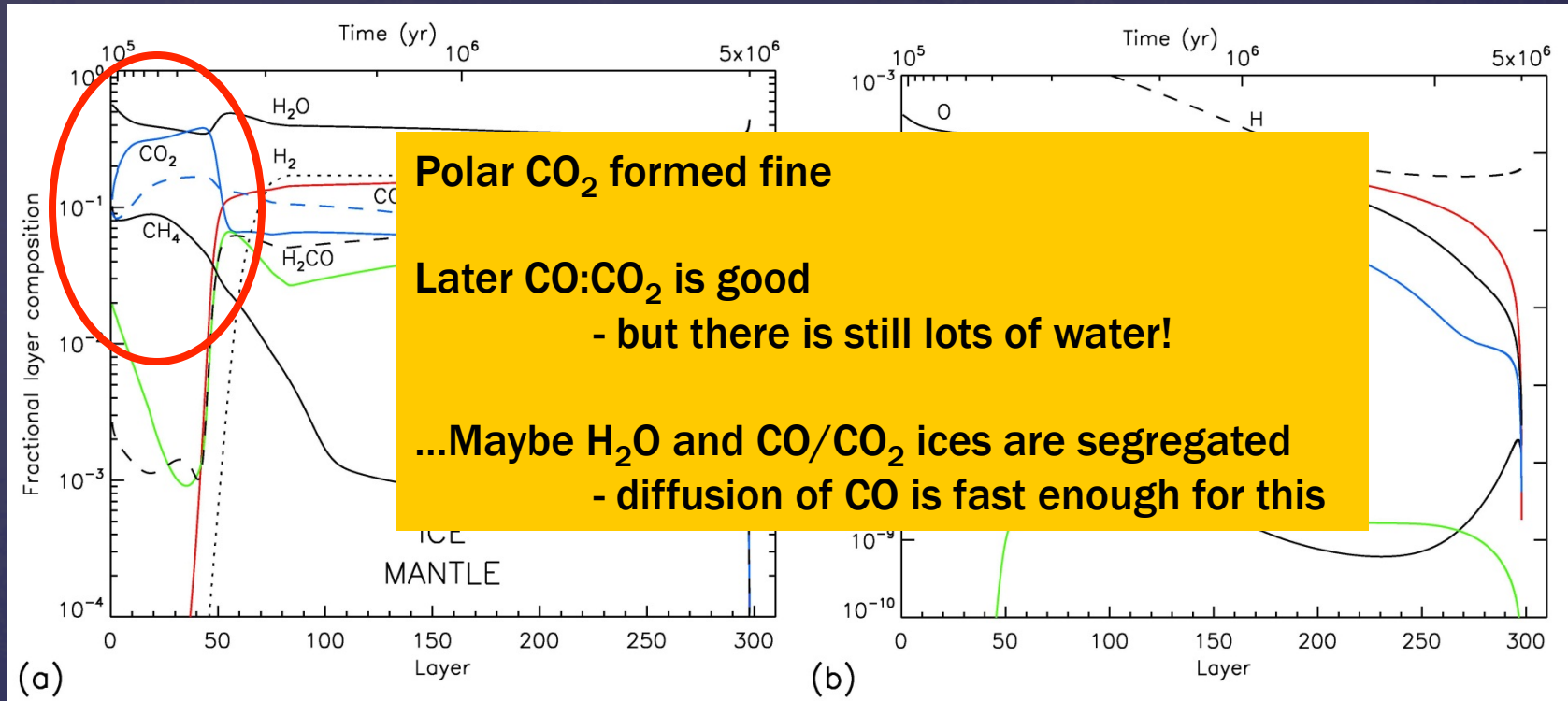
Free-fall collapse (Spitzer 1978/Brown+1988)
$n_H = 3 \times 10^3 \rightarrow 4 \times 10^4$ cm^{-3}
$A_V = 2 \rightarrow 10$
$T_{dust} = \sim18 \rightarrow 8.5$ K

High density collapse (10^7 cm^{-3})

Methanol formation is time-dependent:
   Timescale for ice deposition is crucial
   Slower ice formation → more hydrogenation of CO to methanol

Conclusions

- $CO + OH \rightarrow CO_2 + H$ is capable of forming majority of CO_2 in cold dark clouds

- Sharp switch-over at ~12 K explains CO extinction threshold

- CO_2 , H_2O thresholds related to photodesorption

- At high temps, CO is mobile, reaction proceeds diffusively

- Require low diffusion barriers (<0.4 E_{des})

- At low temps, O + H + CO gives CO_2 – only H mobility is required

- Polar CO_2 and CH_4 well correlated

- Apolar CO_2 may be formed in highly segregated $CO:H_2O$ mixtures

- Methanol ice is formed efficiently when ice build-up is slow

- Need to treat layer formation and activation barriers accurately