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(Lured over to the dark side by Neal  
Evans)

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“....well, if you decide to get involved with episodic accretion then you are probably going to get invited to some pretty whacky conferences..”

Neal Evans (2011)

“...I realised that it (episodic accretion) is probably correct, but it is going to make things very difficult...”

Neal Evans (this morning)

# The Thesis: chemical diagnostics of episodic accretion

- $\text{HCO}^+$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{N}_2\text{H}^+$  ratios can be used to diagnose episodic accretion
- Repeated freeze-out and evaporation leads to a build up of  $\text{CO}_2$ (ice) and perhaps other molecules
- On surfaces:
  - $\text{CO} + \text{O}, \text{OH} \rightarrow \text{CO}_2$
  - Species such as  $\text{CO}$ ,  $\text{OH}$ , etc., evaporate each time, but the  $\text{CO}_2$  is less volatile, so its abundance in the ices can steadily increase
  - Pure  $\text{CO}_2$  indicates the presence of outburst(s)
- Maps of molecular distributions provide fossil maps of episodic luminosity outbursts

# Reasons to be sceptical about the Chemistry

- The nature and efficiencies of gas-grain interactions are not known
  - Freeze-out: OK ?
  - Surface chemistry: no
  - (Thermal) desorption: no
- The physical context of the chemical enhancements is unclear
  - Static, illuminated envelope ?, or collapsing core ?
  - $T(r)$  and  $n(r)$  → excitation/optical depth effects important

- Freeze-out reasonably well-determined  
but probably:

XY



# Consider H<sub>2</sub>O

(*van Dishoeck, Chem. Rev.*)

- ‘Traditional’ dark cloud formation channel:
  - $\text{H}_2 + \text{crp} \rightarrow \text{H}_2^+ + \text{e}^-$
  - $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$
  - $\text{H}_3^+ + \text{O} \rightarrow \text{OH}^+ + \text{H}_2$
  - $\text{OH}^+ + \text{H}_2 \dots \rightarrow \text{H}_3\text{O}^+ + \text{H}$
  - $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}, \text{OH} + \text{H}, \text{H}_2$
- At high temperatures:
  - $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$
  - $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$

# Surface chemistry

- From atomic oxygen:
  - $O + H \rightarrow OH$
  - $OH + H \rightarrow H_2O$
- From  $O_2$ :
  - $[O + O \rightarrow O_2]$
  - $O_2 + H \rightarrow HO_2$
  - $HO_2 + H \text{ (or } H_2) \rightarrow H_2O_2$
  - $H_2O_2 + H \rightarrow H_2O + OH$
  - $OH + H \rightarrow H_2O$

# But...

- Enthalpies of formation of these molecules is large – typically 2-4eV – as compared to physisorption binding energies  $\leq 0.1\text{eV}$ .
- e.g.  $2\text{H} \rightarrow \text{H}_2 + 4.5\text{eV}$ : shared between translational, vibrational, rotational and thermal modes (c.f. adsorption energy  $\sim 1000\text{K} = 0.08\text{eV}$ )
- Experiments *always* show significant desorption on formation, yet...
- If  $\text{H}_2\text{O}$  is allowed to desorb, even at low levels, too much gas-phase  $\text{H}_2\text{O}$  is predicted

# The case of CO<sub>2</sub>

- Believed to be formed by the surface reaction:-  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$
- But where does the OH come from.....?  
 $\text{O} + \text{H} \rightarrow \text{OH} + 4.77\text{eV}$
- If the OH is chemisorbed, then it is not surface mobile.....

# Thermal desorption

- Rate:  $k = \nu_j [N_i]^j \exp(-E_{\text{bind}}/kT_{\text{dust}})$
- $j$  is the reaction order (usually taken to be 0)
- $\nu_j$  is the vibration frequency  $\propto (E_{\text{bind}}/m_i)^{0.5}$
- Exponential function  $\rightarrow$  for each species can define a temperature ( $T_{\text{evap.}}$ ) above which the species is completely desorbed.
- Balancing freeze-out with thermal desorption:  
$$T_{\text{evap}} \sim T_{\text{bind}} / (52 - \ln n_i + 0.5 \ln(T_{\text{bind}}/T_{\text{gas}}))$$

# But things may not be so simple...

*Viti, Collings...McCoustra*

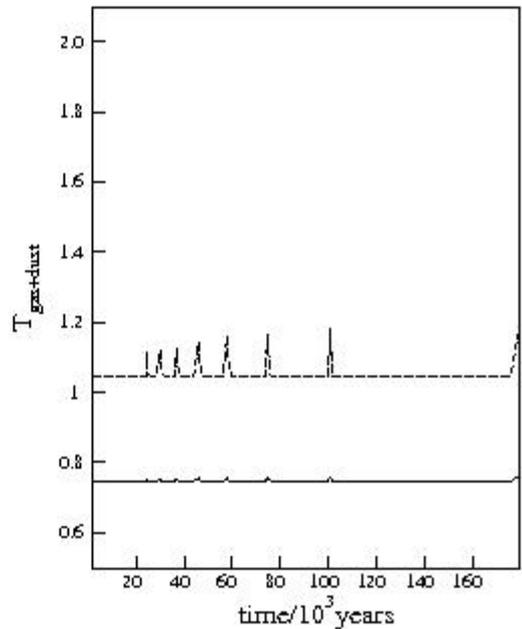
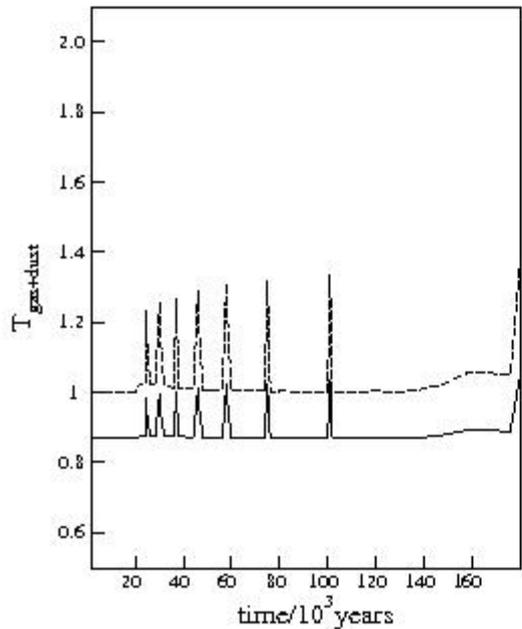
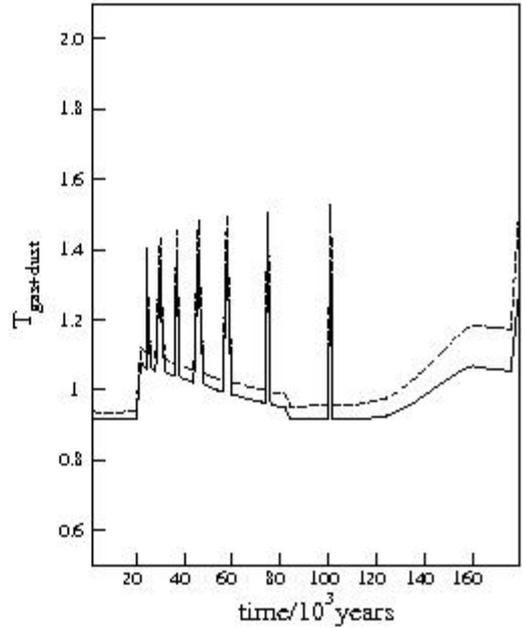
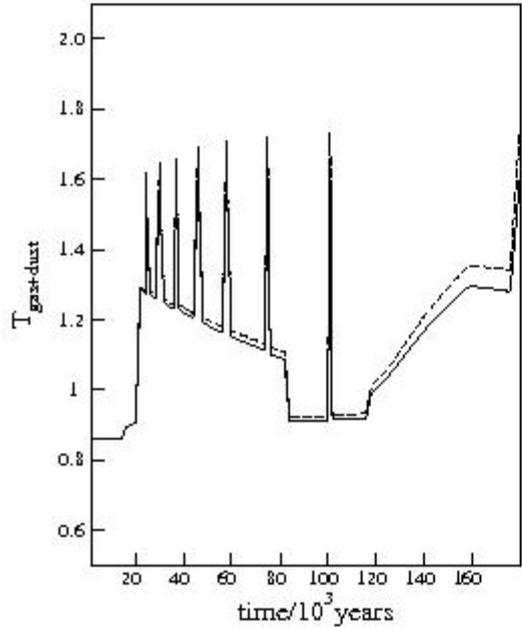
- Monotonic heating leads to a sequence of desorption 'spikes'
- Species can be:-
  - CO-like: CO, N<sub>2</sub>, O<sub>2</sub>....
  - Intermediate: HCN, H<sub>2</sub>S, CO<sub>2</sub>....
  - H<sub>2</sub>O-like: H<sub>2</sub>O, H<sub>2</sub>CO, CH<sub>3</sub>OH....
  - Reactive: C<sub>2</sub>H, OCN, H<sub>2</sub>CN....
  - Refractory: Mg, S<sub>2</sub>
- Desorption bands:
  - Pure species
  - Monomolecular layer on H<sub>2</sub>O
  - Amorphous-crystalline conversion of H<sub>2</sub>O ( 'volcano' )
  - CO-desorption when H<sub>2</sub>O desorbs ( 'co-desorption' )
  - Desorption from bare grains

# A comprehensive model...

*(Rawlings, Evans et al.)*

- Multi-point, Lagrangian flow
- Initial conditions: quasi-static contraction [Keto, Caselli, Rawlings...2010-14] equivalent to PPC phase
- ‘standard’ inside-out collapse (equivalent to Class 0 phase)
- Variable luminosity central source →  
 $T_{\text{gas}}(t,r), T_{\text{dust}}(t,r)$

Log ( $T_{\text{gas}}$ ) – solid lines  
and Log ( $T_{\text{dust}}$ ) –  
dashed lines, as  
functions of time for  
four positions between  
0.004 and 0.15pc



- Establishes an ‘onion-skin’ chemically layered structure, with layers defined by  $T_{\text{des}}(i)=T_{\text{dust}}(t,r)$ .
- Between ‘flashes’, the gas flows through these shells and chemically evolves
- BUT, there may be timescale issues (light propagation time, dust heating timescale etc.)
- In this model: instantaneous desorption at  $T_{\text{des}}(i)$ ; species-by-species
- Lots of free parameters:  $M_{\text{cloud}}, R_{\text{cloud}}, t_{\text{cloud}}$   
 $F_{\text{UV}}, \zeta_{\text{cr}}, A_{\text{v}}(\text{ext.}), \langle r_{\text{dust}} \rangle, \sigma_{\text{g}}, \kappa_{\text{dust}}$   
 continuous absorption mechanisms/efficiencies
- Efficiencies:
  - $\text{O}, \text{O}^+, \text{OH} \rightarrow \text{CO}_2$
  - $\text{O}, \text{O}^+, \text{OH} \rightarrow \text{H}_2\text{O}$
  - $\text{O}_2 \rightarrow \text{H}_2\text{O}$  etc.

- Essential result:
- Abundances (e.g. of CO<sub>2</sub>) are very sensitive to the chosen values of the ‘free’ parameters, most significantly (not surprisingly) the assumptions about the surface chemistry efficiencies.
- This applies to other species as well
- BUT the models do at least predict unusually high abundances of CO<sub>2</sub> and anomalous abundances of gas phase species etc.
- Search for species/anomalies that are *unique* to the episodic accretion scenario