

Speciation, location, and reactivity of aldehydes in snow

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A sunset over the ocean with large 3D numbers overlaid. The number 1984 is yellow and orange, 1999 is white with a black outline, and 2012 is blue. The background shows a sunset over the ocean with a cloudy sky.


1984 1999 2012

Honrath et al. (1999)

Evidence of NO_x production within or upon ice particles in the Greenland snowpack

Sumner and Shepson (1999)

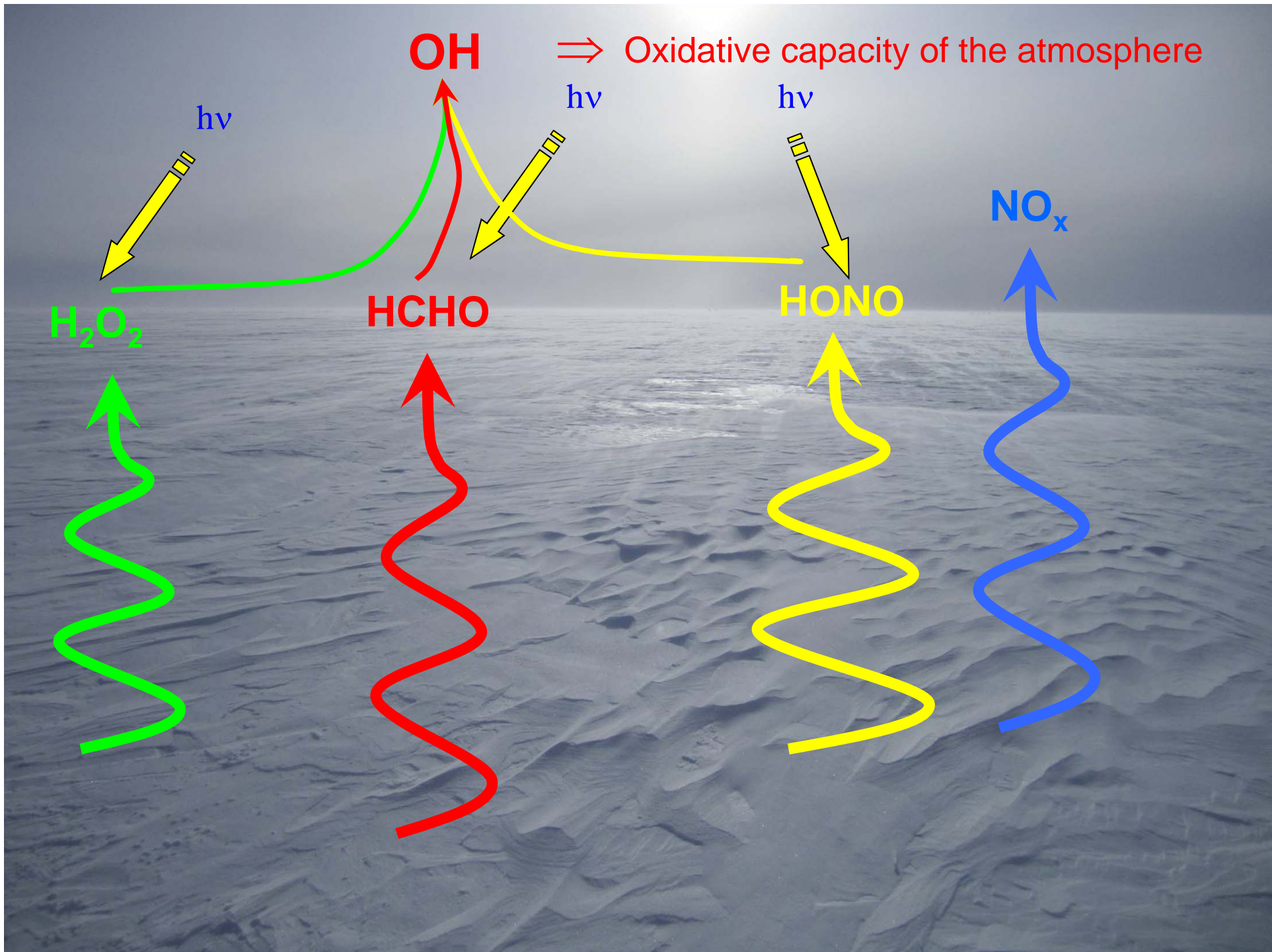
Snowpack production of formaldehyde and its effect on the Arctic troposphere



Useless cold
white powdery
stuff

**Exciting novel
scientific topic !!**

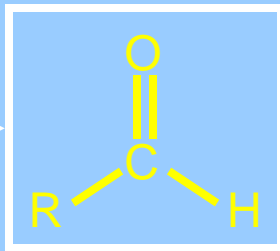
(that can be funded)



Aldehydes in the polar atmosphere

Lifetime for common aldehydes:
mins to hours

Aldehydes in polar environments
can be produced locally



Direct
emissions

OH oxydation

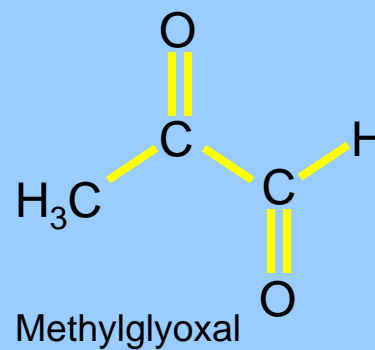
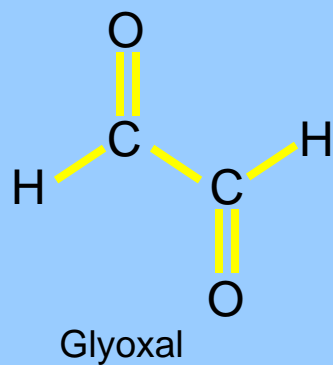
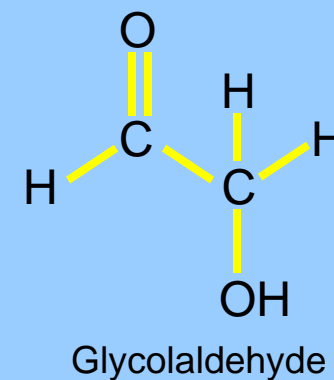
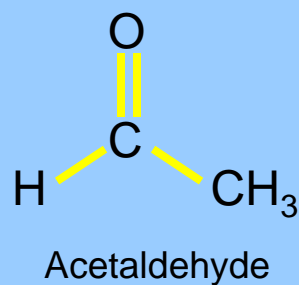
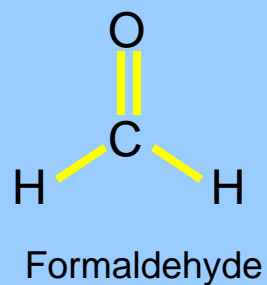
VOCs

Aromatics, ...

Isoprene
Terpenes, ...



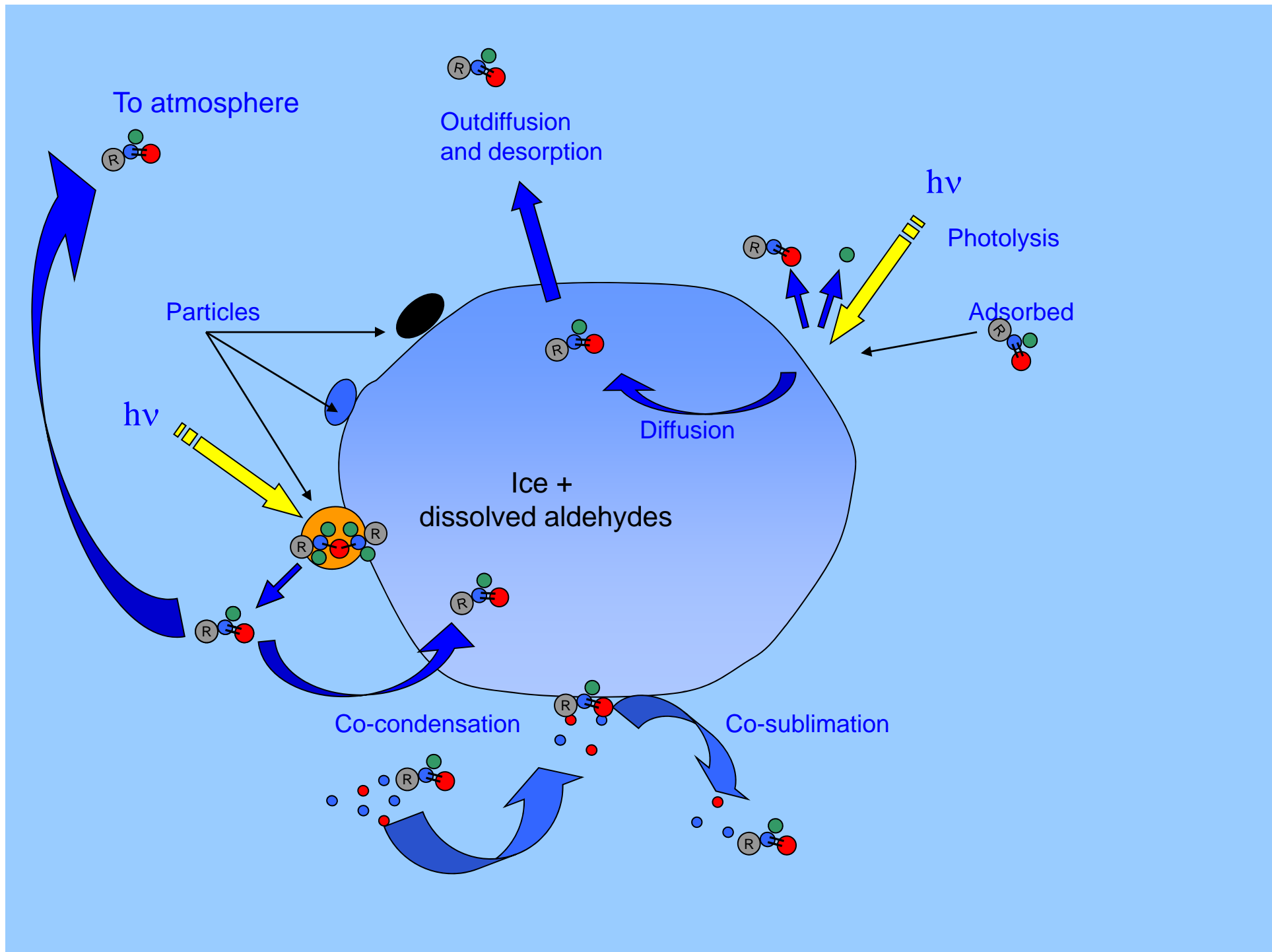
Aldehydes of interest



- OH source
- Involved in secondary aerosol production

Questions about Aldehydes

- Which aldehydes are present in snow ?
- Where are they located in snow ?
- What is their reactivity ?
- What are the processes of exchange with the atmosphere ?



The case of HCHO – known lab data

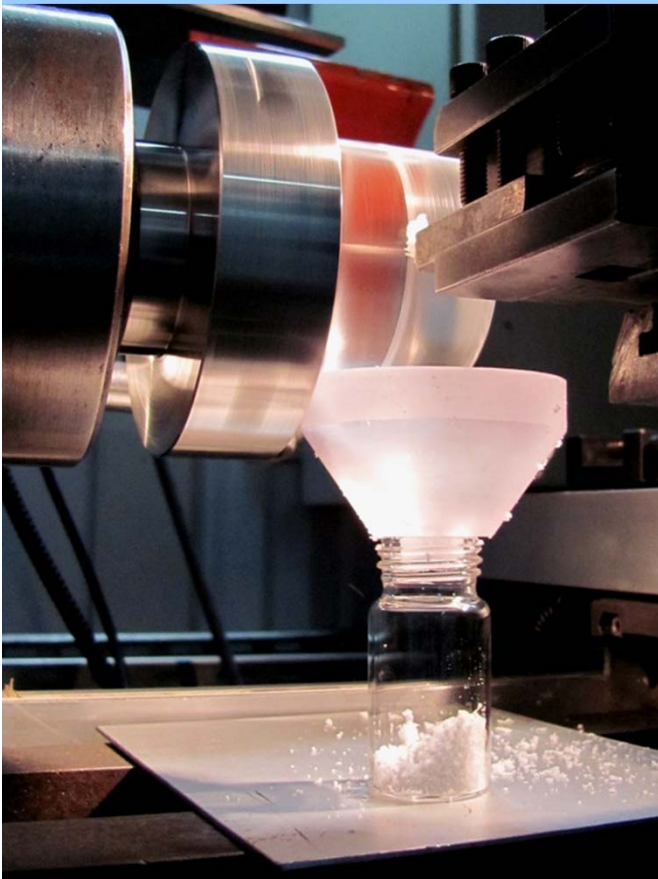
1- Adsorption is weak

2- Formation of an ice-HCHO solid solution

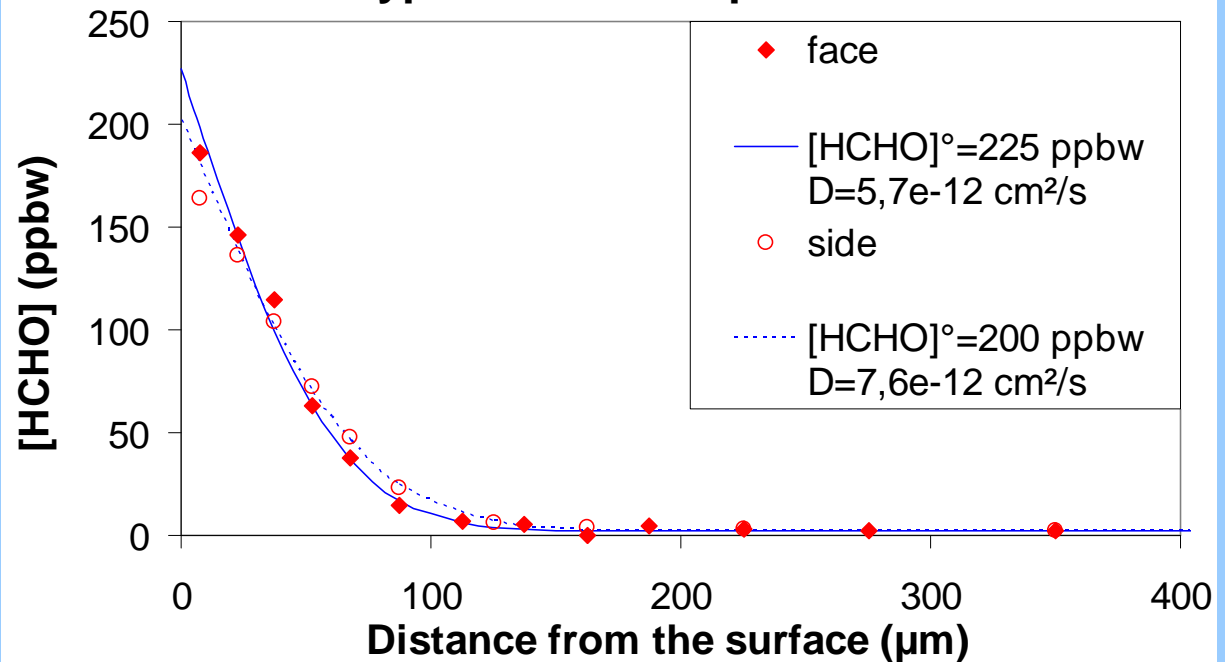
Ice single crystal exposed to P_{HCHO}

Serial sectioning on lathe in cold room

$$X_{HCHO}(x,t) = X_{HCHO}^0(T, P_{HCHO}) \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_{HCHO}t}} \right) \right]$$



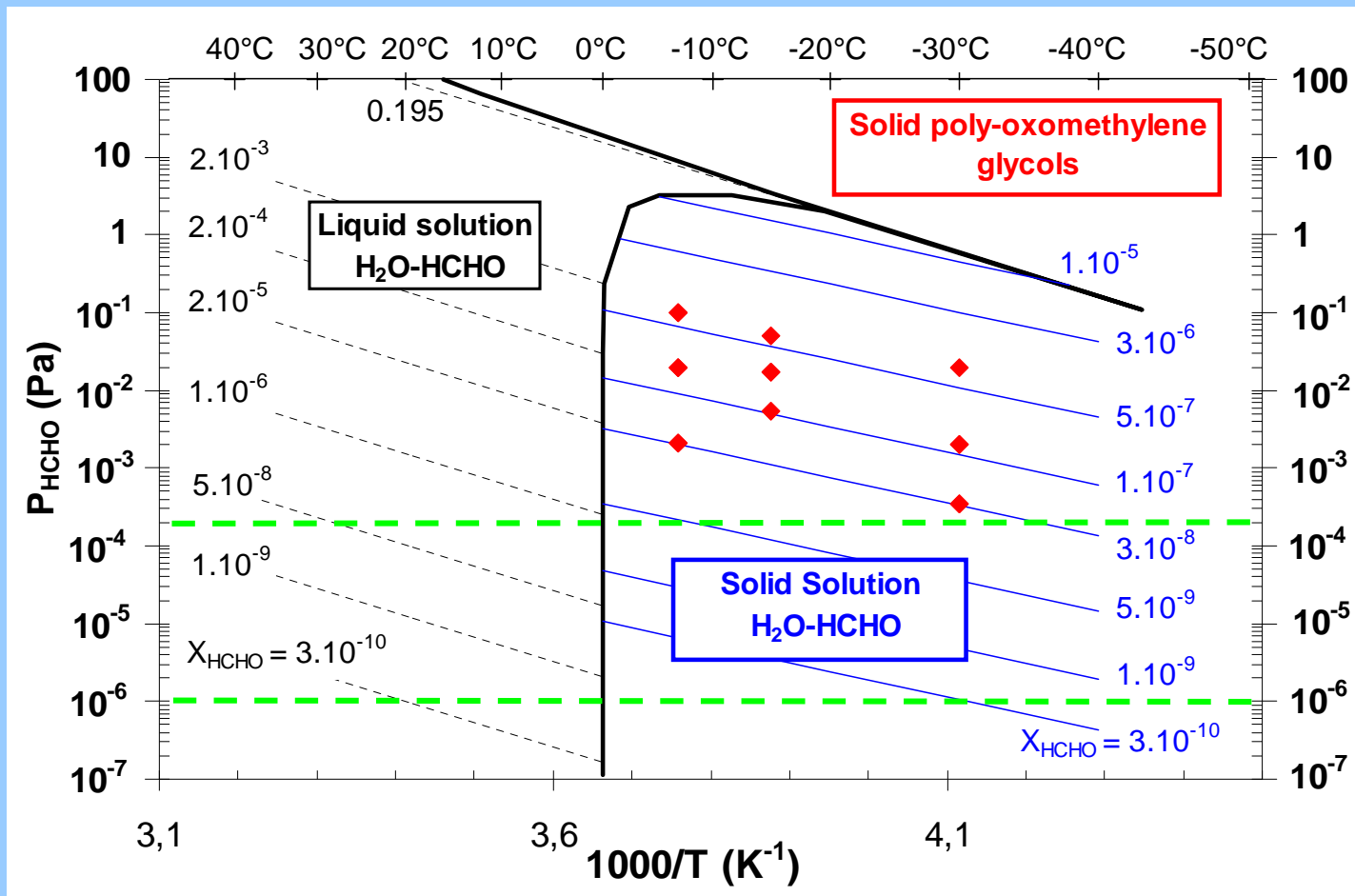
Typical diffusion profile



HCHO – H₂O phase diagram

$$X_{HCHO,ice} = 9.898 \times 10^{-13} e^{(4072/T)} (P_{HCHO})^{0.803}$$

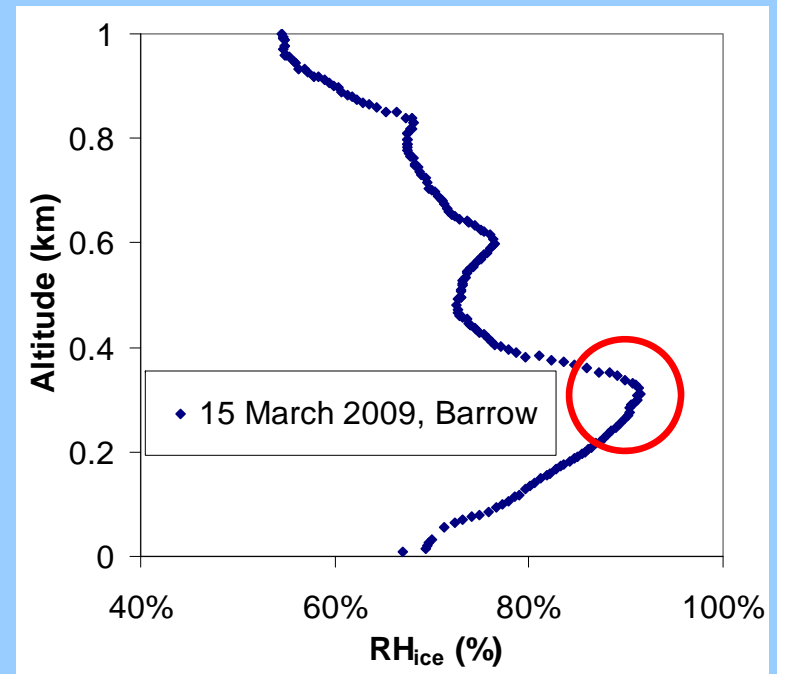
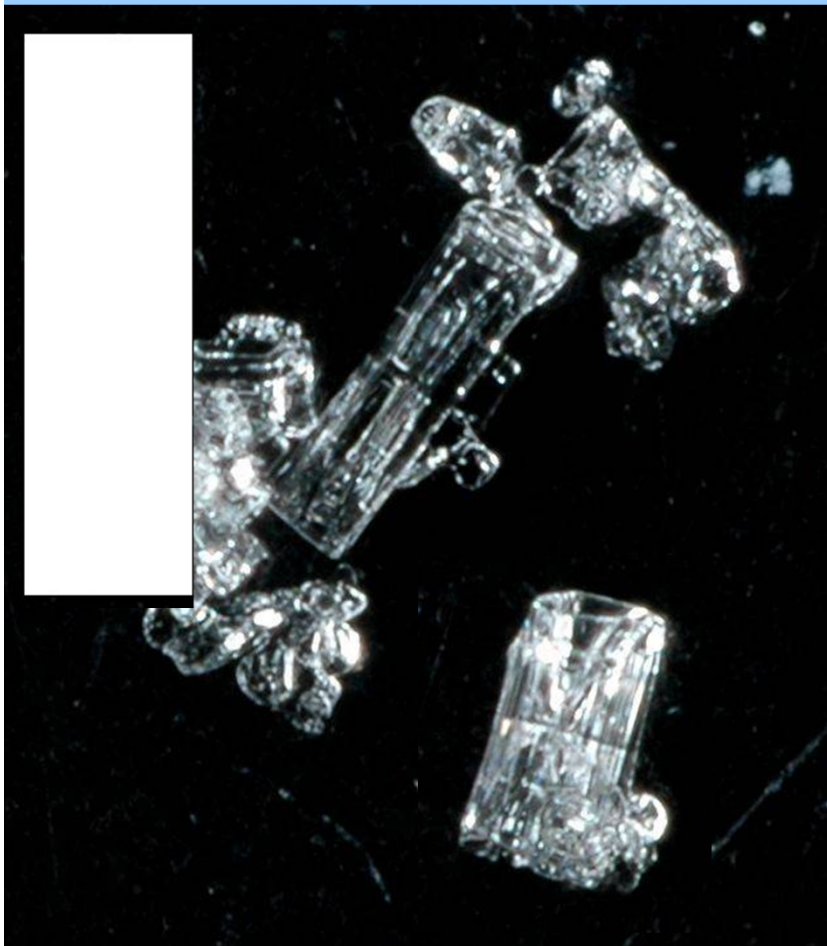
$$\Delta h_{sub,HCHO} = 42.15 \pm 2.38 \text{ kJ/mol}$$



Equilibrium of polar snow

Diamond dust : clear sky precipitation

Submillimetric crystals that form at ~ 200 m

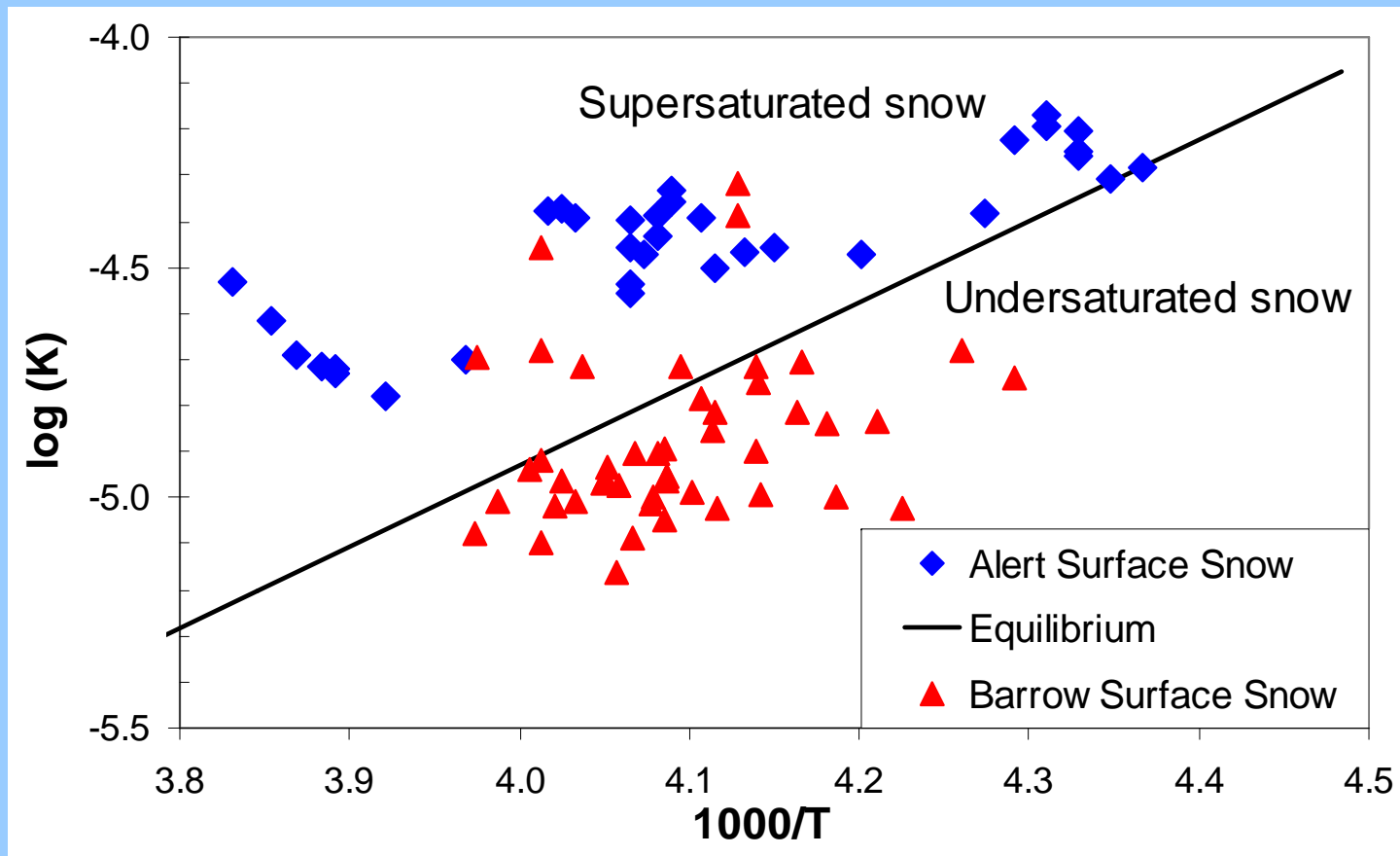


Equilibrium of polar snow

Alert : Supersaturated

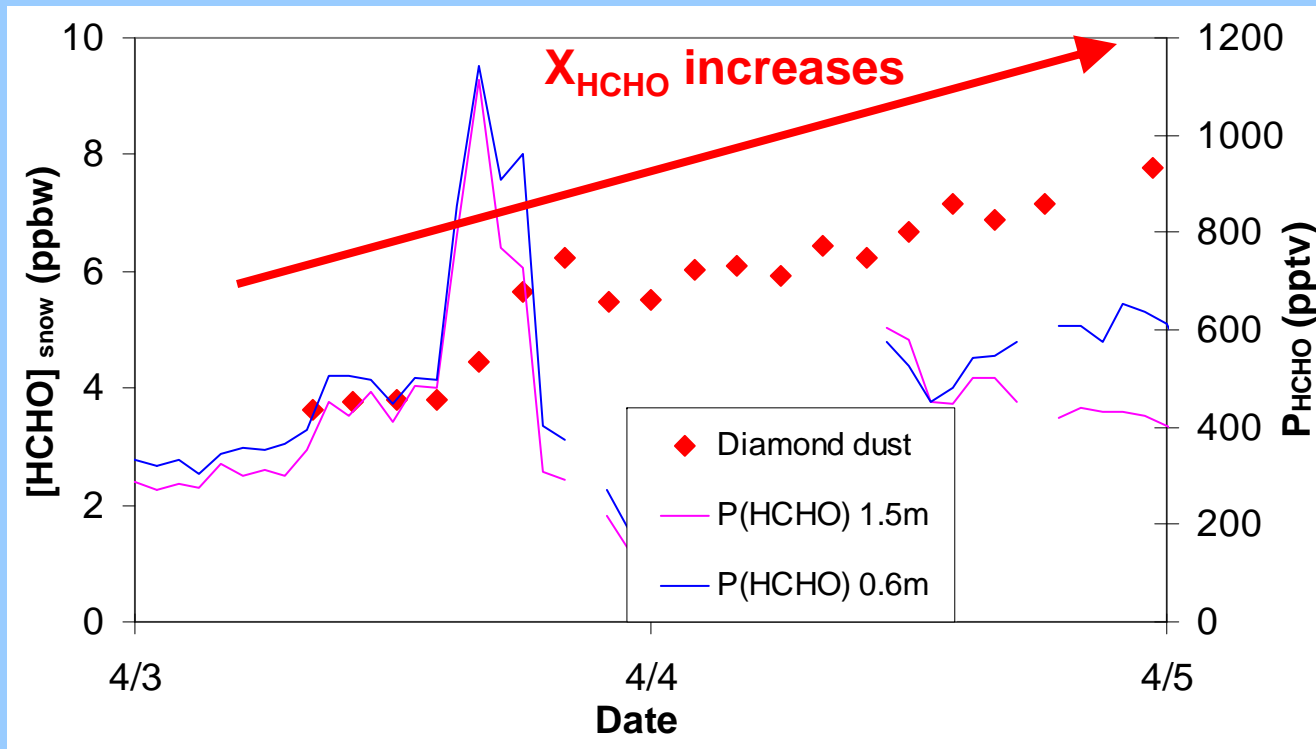
Barrow : Undersaturated

More active Br
chemistry at Barrow

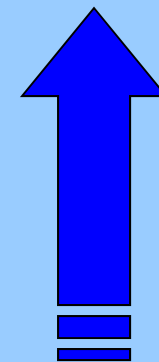


Evolution of Barrow surface snow

- Measure :
- Snow SSA $SSA = 90 \text{ m}^2 \text{ kg}^{-1}$, $R_e = 41 \text{ }\mu\text{m}$
 - $X_{\text{HCHO, snow}}$
 - P_{HCHO} , 3 heights



Upward HCHO flux



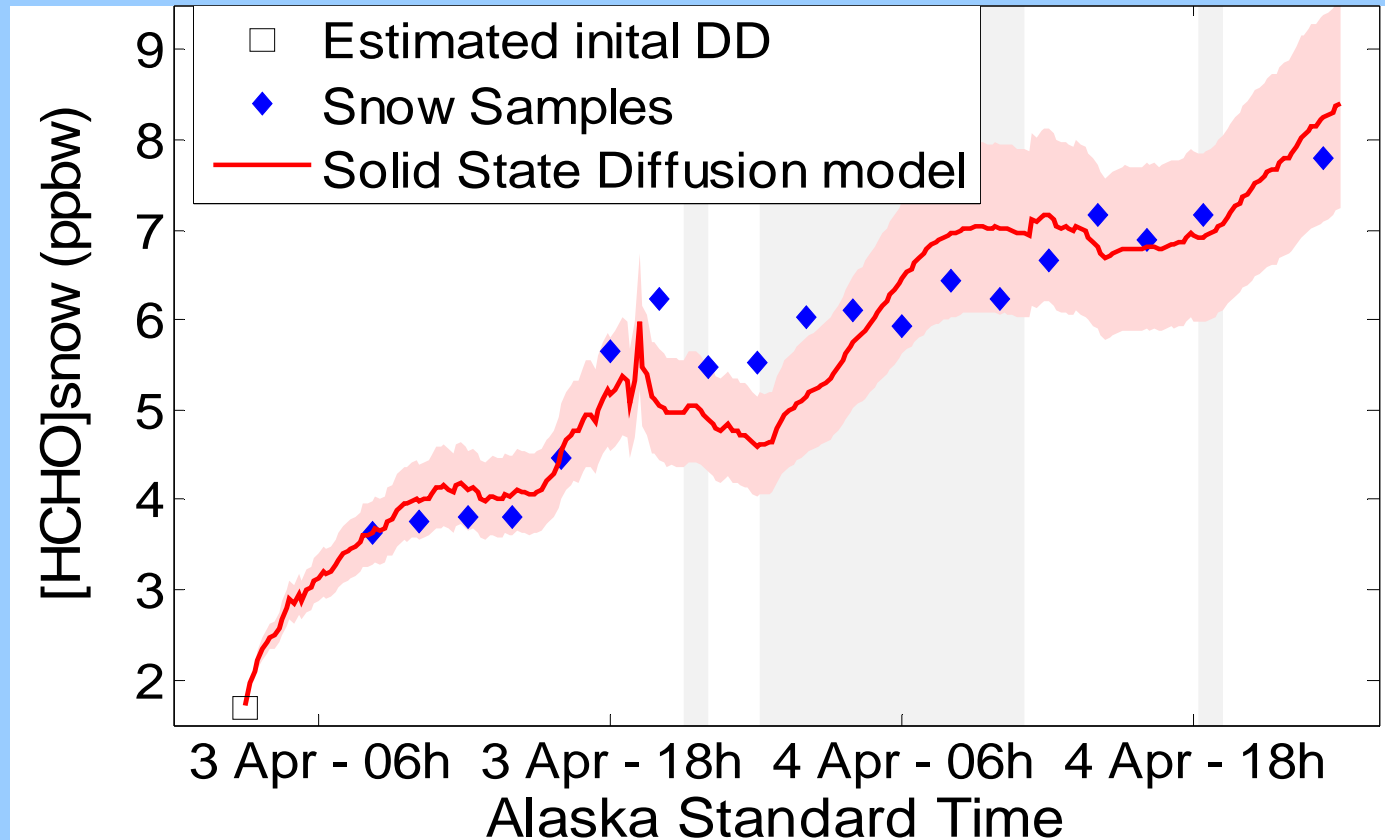
⇒ There is an HCHO source in the snow, most likely photochemical

Solid state diffusion model

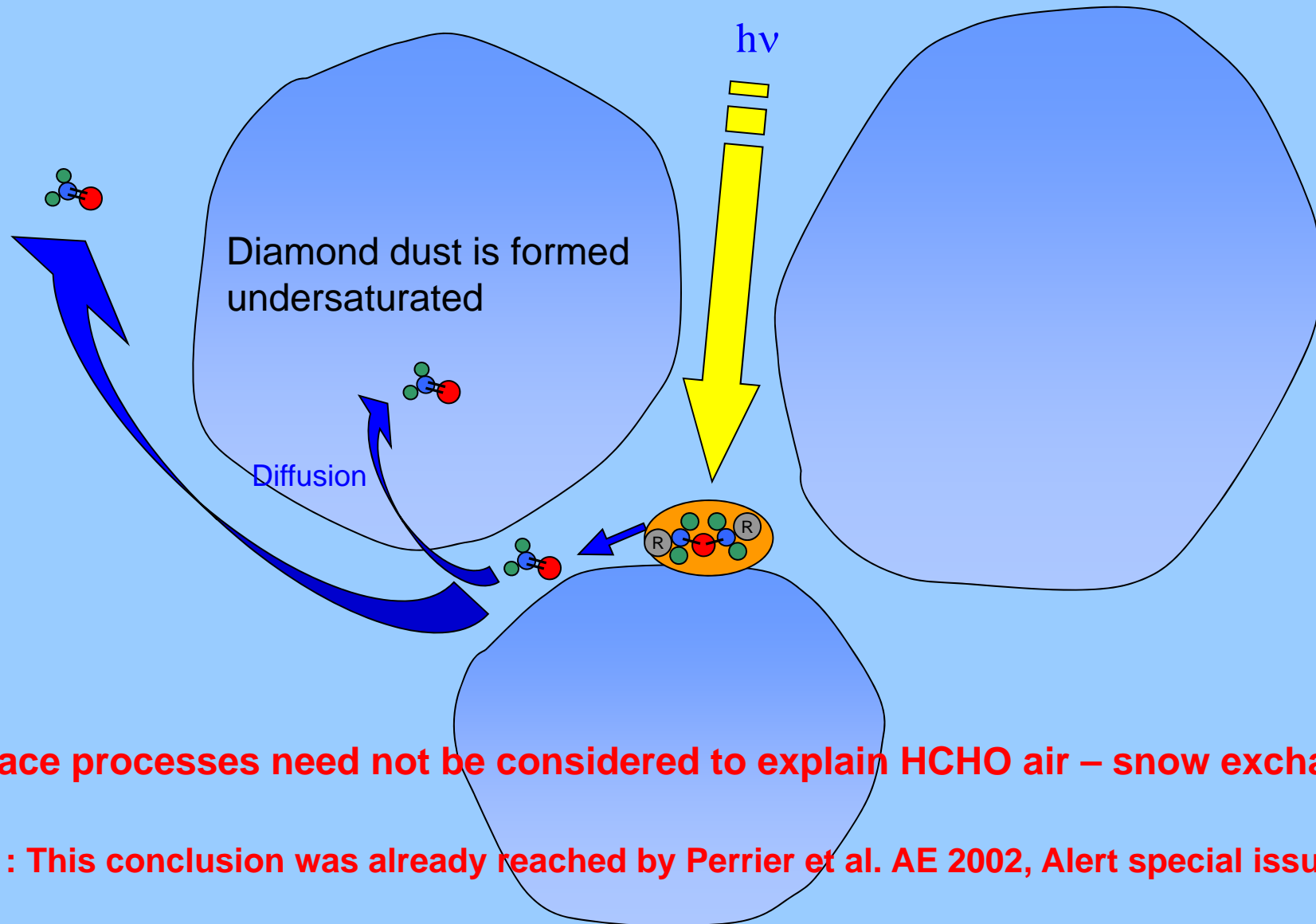
Diamond dust : $SSA = 90 \text{ m}^2 \text{ kg}^{-1}$, $R_e = 41 \text{ }\mu\text{m}$

P_{HCHO} = value measured at 0.6 m

Solid state diffusion into spheres, $D_{\text{HCHO}} = 6 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$



Conclusion on HCHO air-snow exchange



Surface processes need not be considered to explain HCHO air – snow exchanges

Note : This conclusion was already reached by Perrier et al. AE 2002, Alert special issue

What about other aldehydes ?

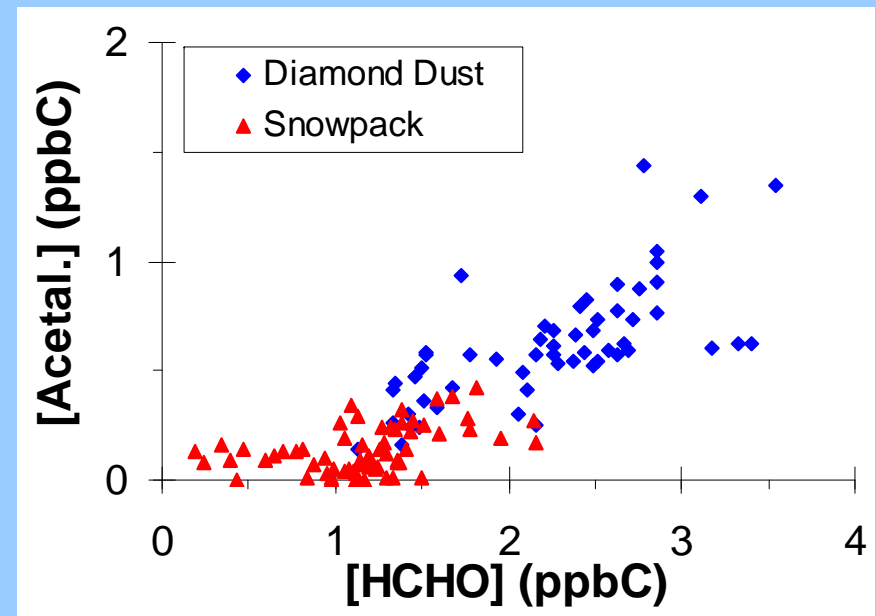
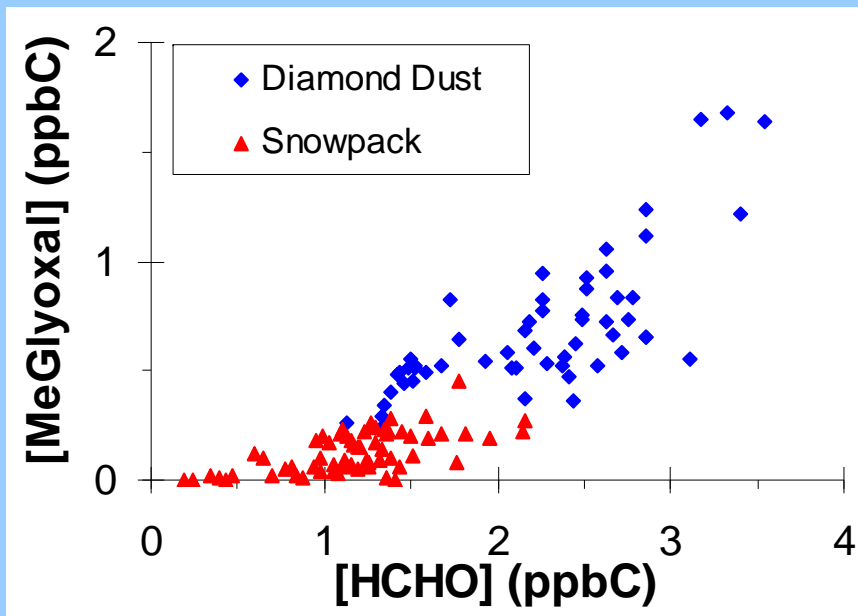
Acetaldehyde, glyoxal and methylglyoxal all correlated with formaldehyde

⇒ Similar formation process: photochemistry of organic particles

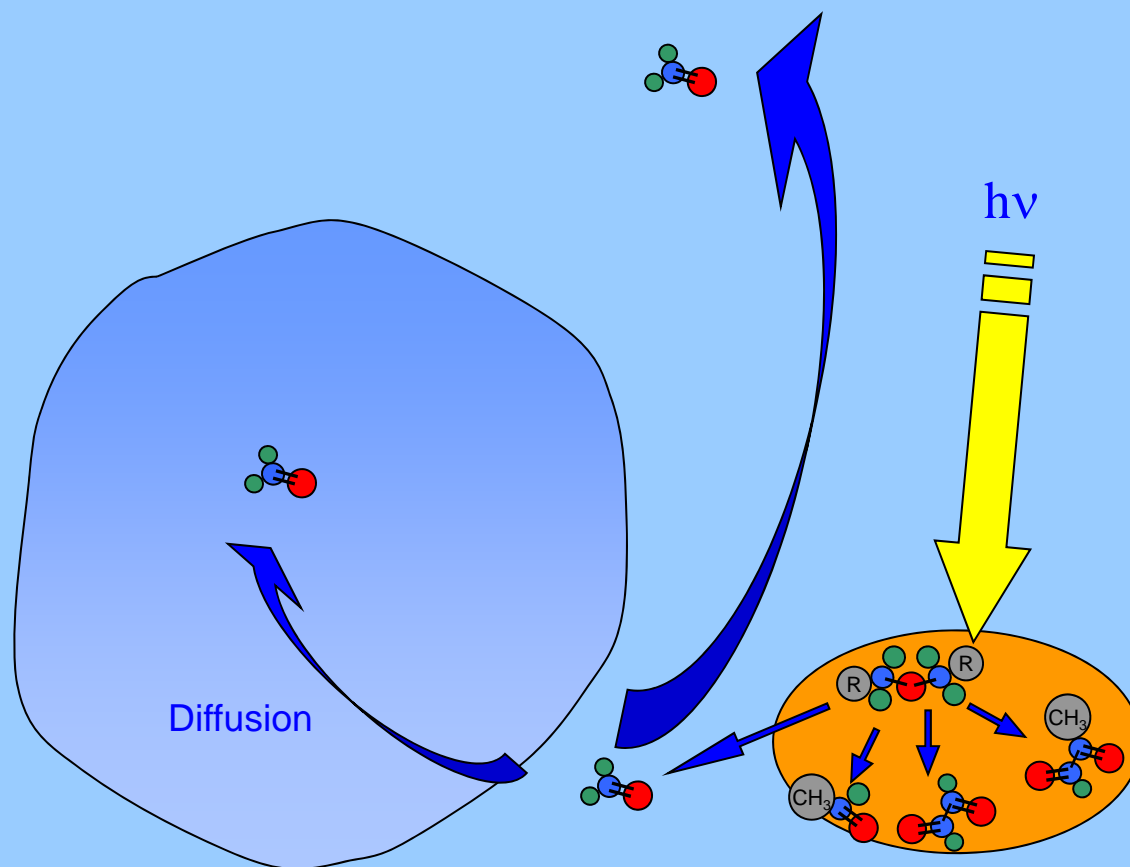
Adsorbed ?

Dissolved ?

⇒ In organic particles (?)



Aldehyde production in snow



To understand aldehyde production: organic particles composition and reactivity

To understand aldehyde emissions: diffusion and solubility, particle thermodynamics