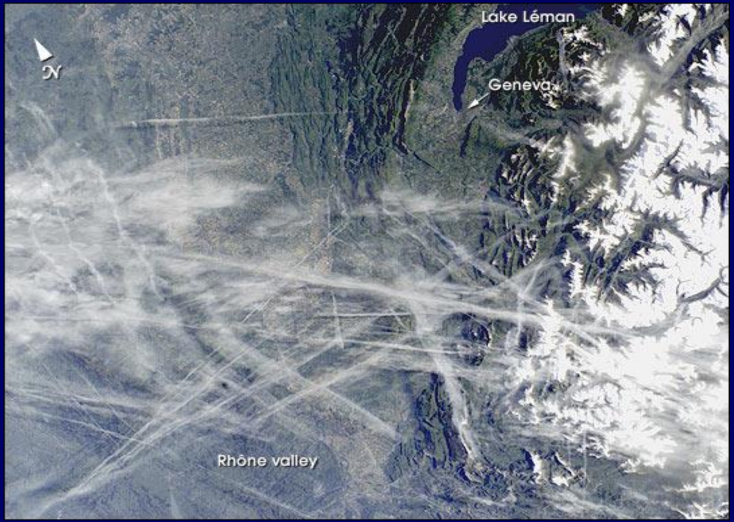
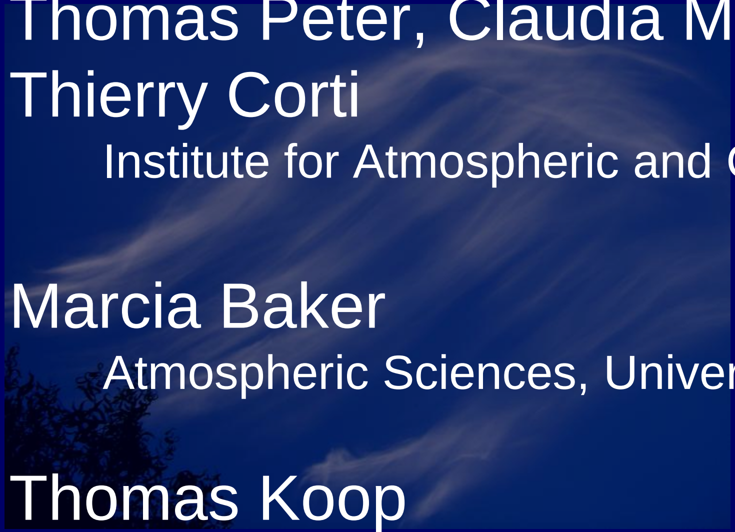
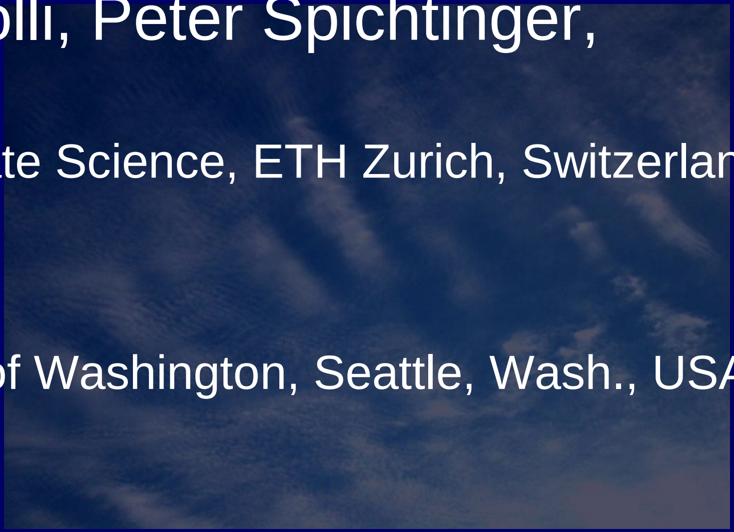
The High Supersaturation Puzzle



The High Supersaturation Puzzle





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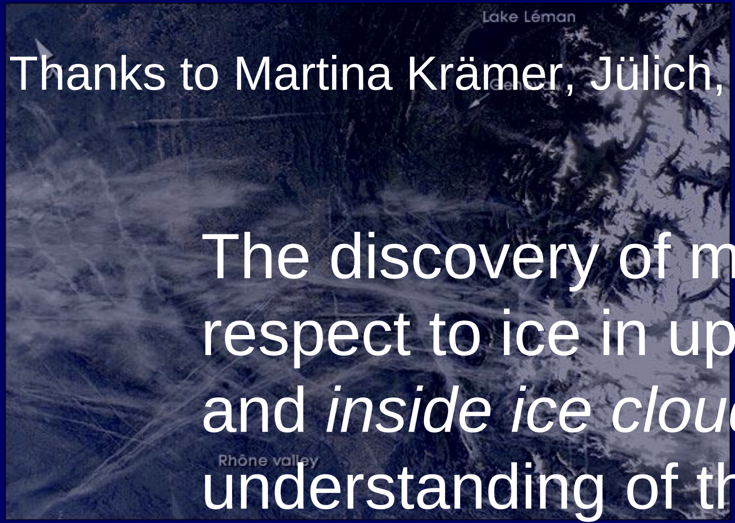
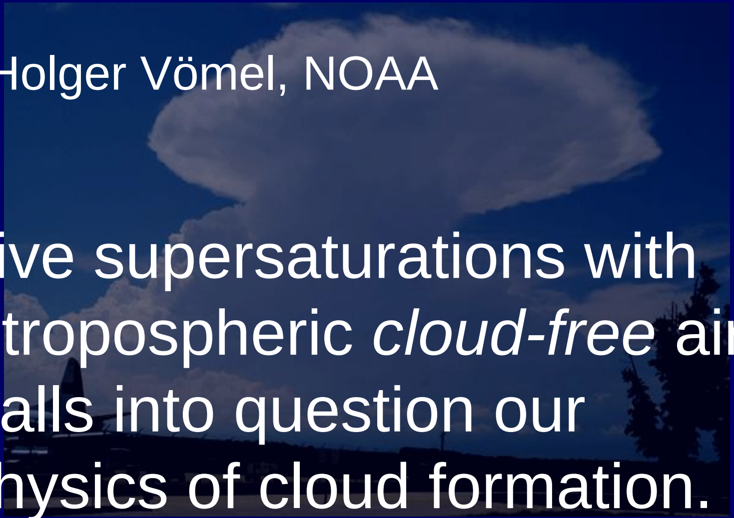




Thanks to Martina Krämer, Jülich, and Holger Vömel, NOAA

The discovery of massive supersaturations with respect to ice in upper tropospheric *cloud-free* air and *inside ice clouds* calls into question our understanding of the physics of cloud formation.

Saturation ratio with respect to ice:

$$S = \frac{p_{H_2O}}{p_{vap}(T)} = \frac{n_{H_2O}}{n_{vap}(T)}$$

p_{H_2O} = partial pressure of water

$p_{vap}(T)$ = vapor pressure of ice

$S > 1$ → ice particles grow

$S = 1$ → ice particles are in equilibrium with the gas phase

$S < 1$ → ice particles evaporate

$s = S - 1$ → supersaturation

Relative humidity wrt ice: RHI = S

$S = 1$ RHI = 100 %

Saturation ratio with respect to ice:

$$S = \frac{p_{\mathrm{H_2O}}}{p_{\mathrm{vap}}(T)} = \frac{n_{\mathrm{H_2O}}}{n_{\mathrm{vap}}(T)}$$

$p_{\mathrm{H_2O}}$ = partial pressure of water

$p_{\mathrm{vap}}(T)$ = vapor pressure of ice

Arrhenius-type expression for vapor pressure:

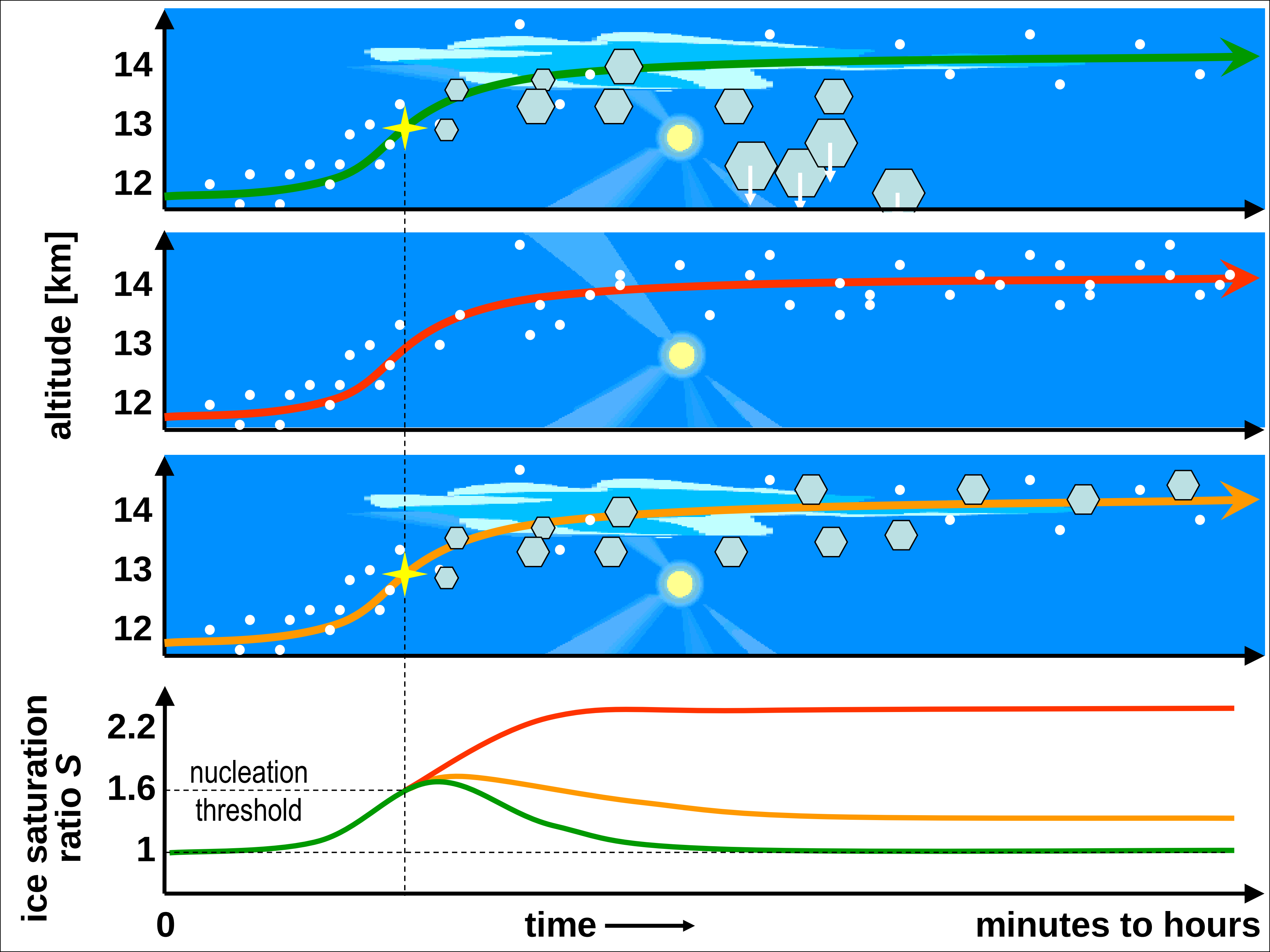
$$p_{\mathrm{vap}}(T) = A\, e^{-B/T}$$

Two questions central to our understanding of ice cloud formation:

Nucleation and uptake kinetics:

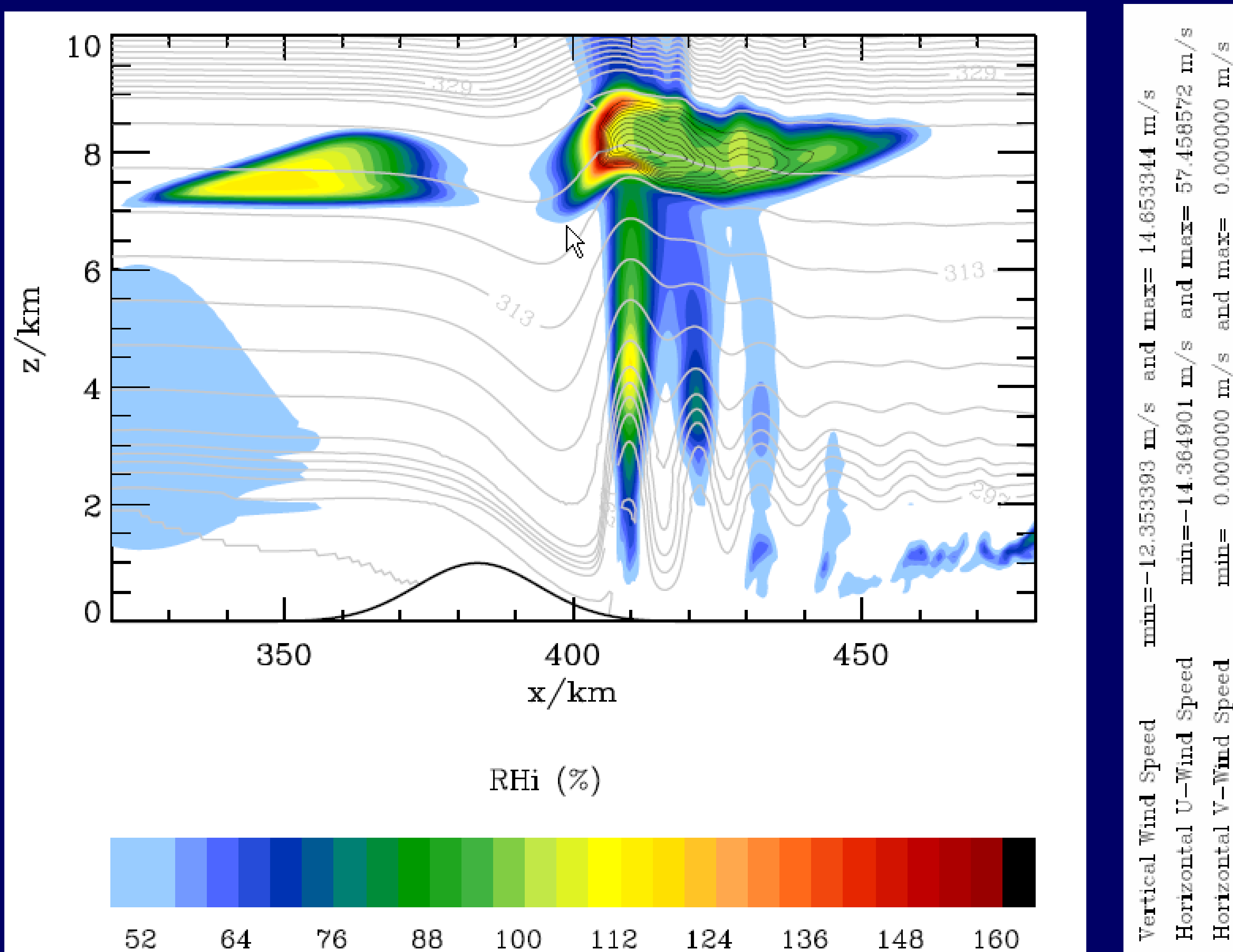
(1) At what *S* do we expect ice to nucleate?

(2) Thereafter, how rapidly do we expect ice to grow and *S* to equilibrate (*S*   1)?

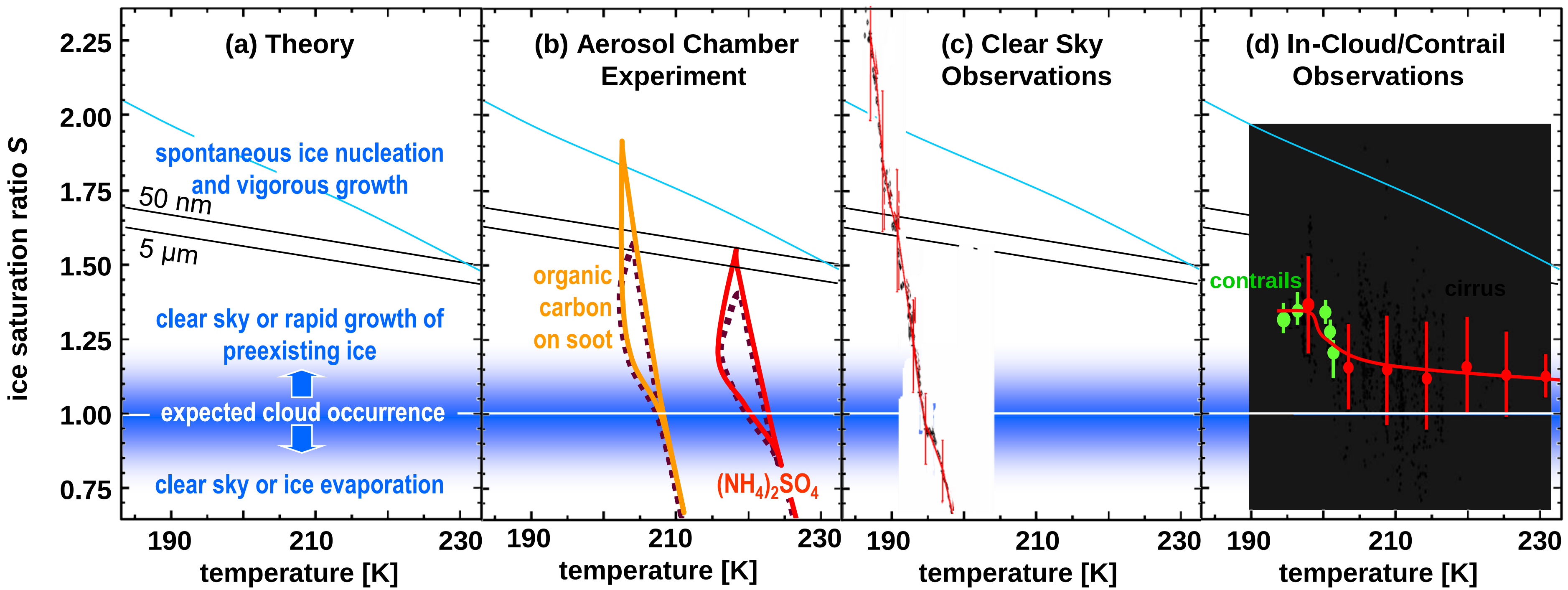


altitude [km]
14
13
12
14
13
12
14
13
12
ice saturation ratio S
2.2
1.6
1
nucleation
threshold
0
time
minutes to hours

How do we expect *S* in a cirrus to develop dynamically?



The supersaturation puzzle – the observations



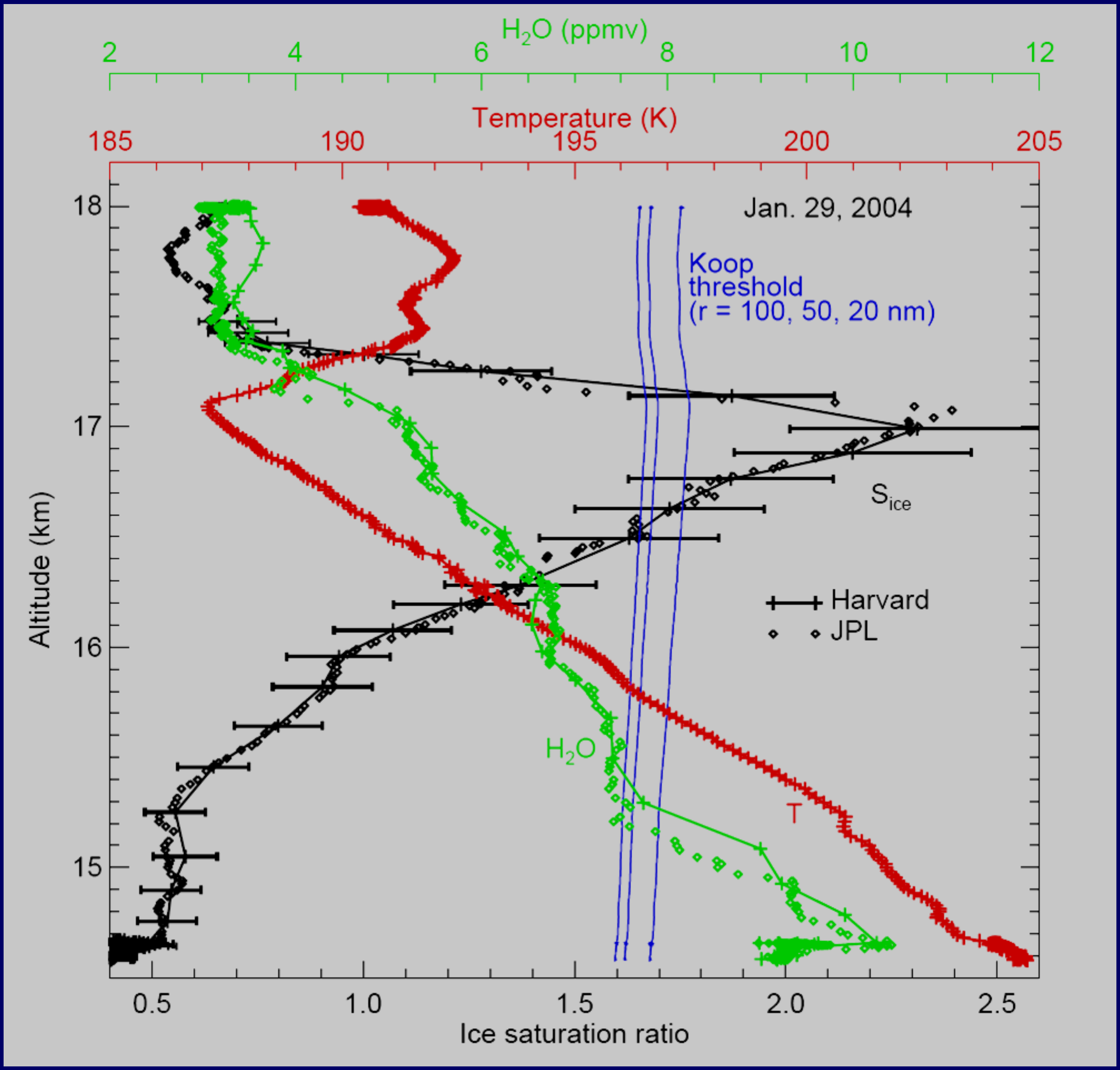
Koop et al., Nature, 2000

Möhler et al., Meteorol. Zs., 2005, Abbatt et al., Science, 2006

Jensen et al., Atmos. Chem. Phys., 2005

Gao et al., Science, 2004

Jensen et al., Atmos. Chem. Phys., 2005



Pre-AVE campaign: Measurements made during the descent of WB-57:

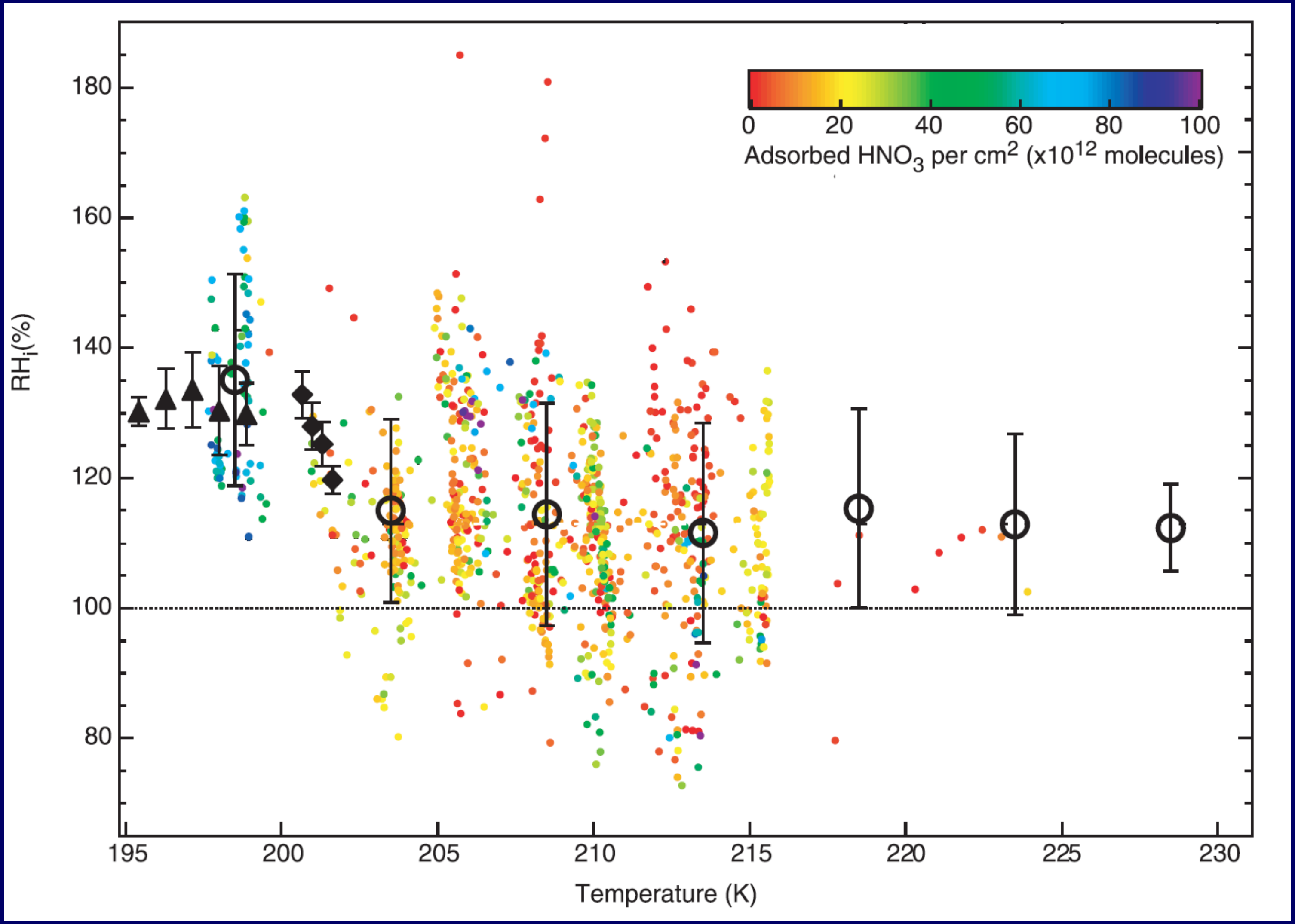
log-normal aerosol size distribution with

$n = 100\ cm^{-3}$,

$r_m = 0.025\ \mu m$,

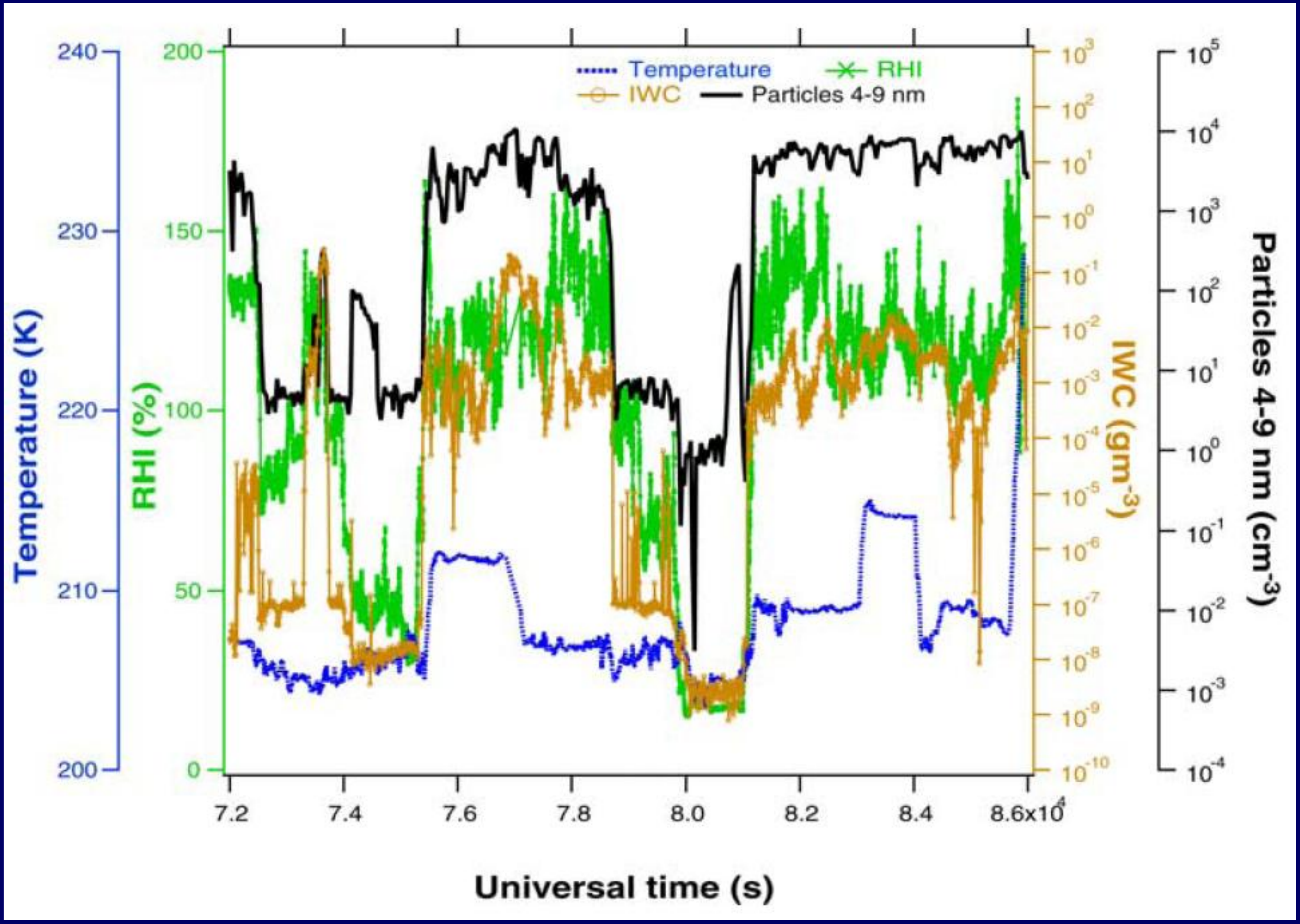
= 1.4.

Gao et al., Science, 2004



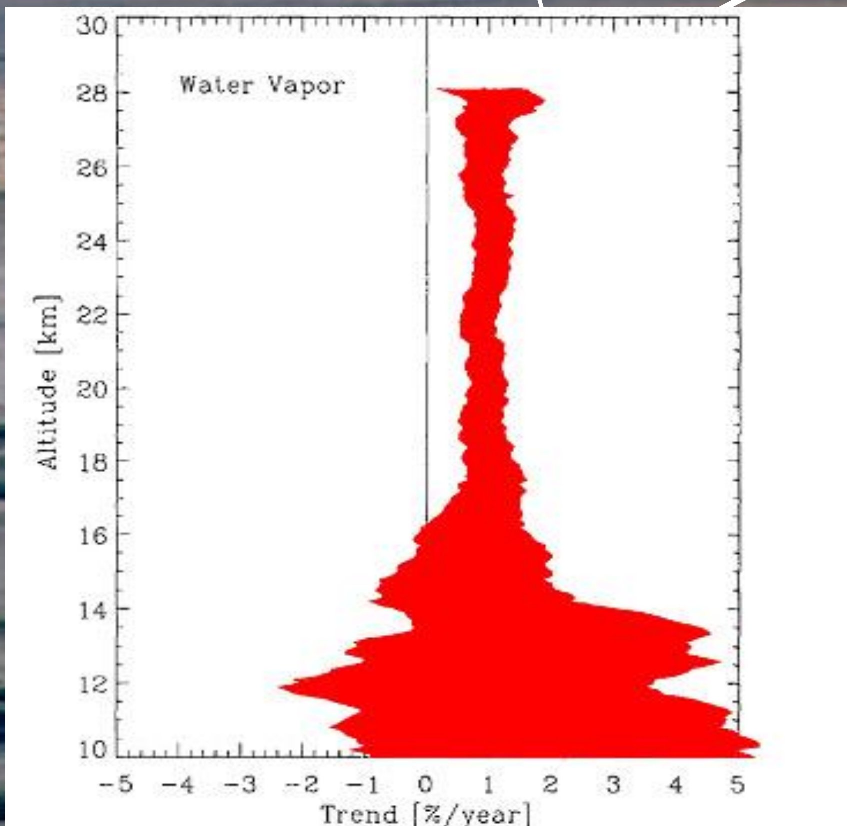
5-K averages, all flights

Lee et al., JGR, 2004:



Measured temperature (blue), RHI (green), IWC (orange), and N4–9 (black) on 23 July 2002 during CRYSTAL-FACE. Temperature and RHI are 1-s averages, IWC is a 10-s average, and N4–9 is a 30-s average.

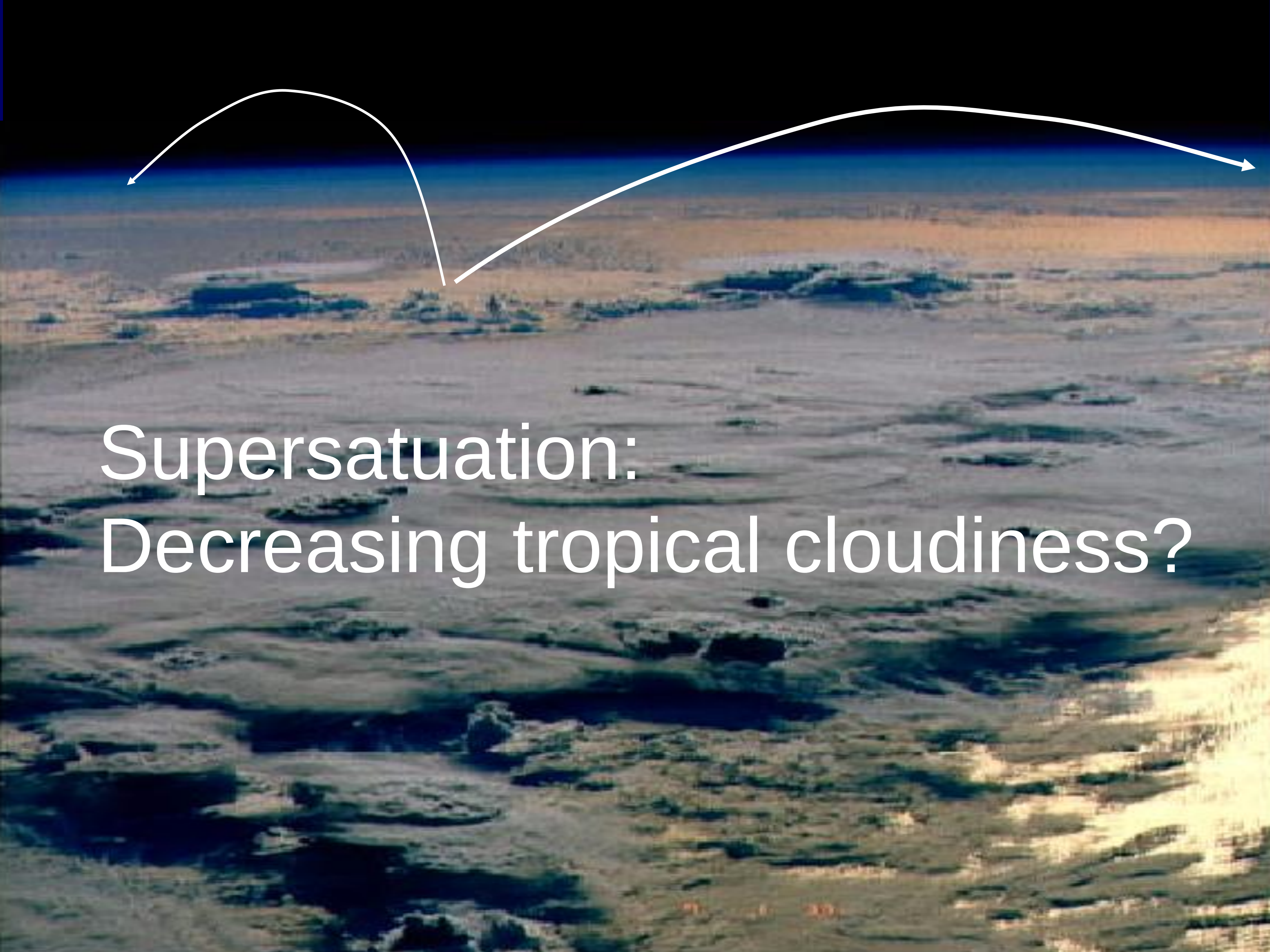
Increasing stratospheric humidity



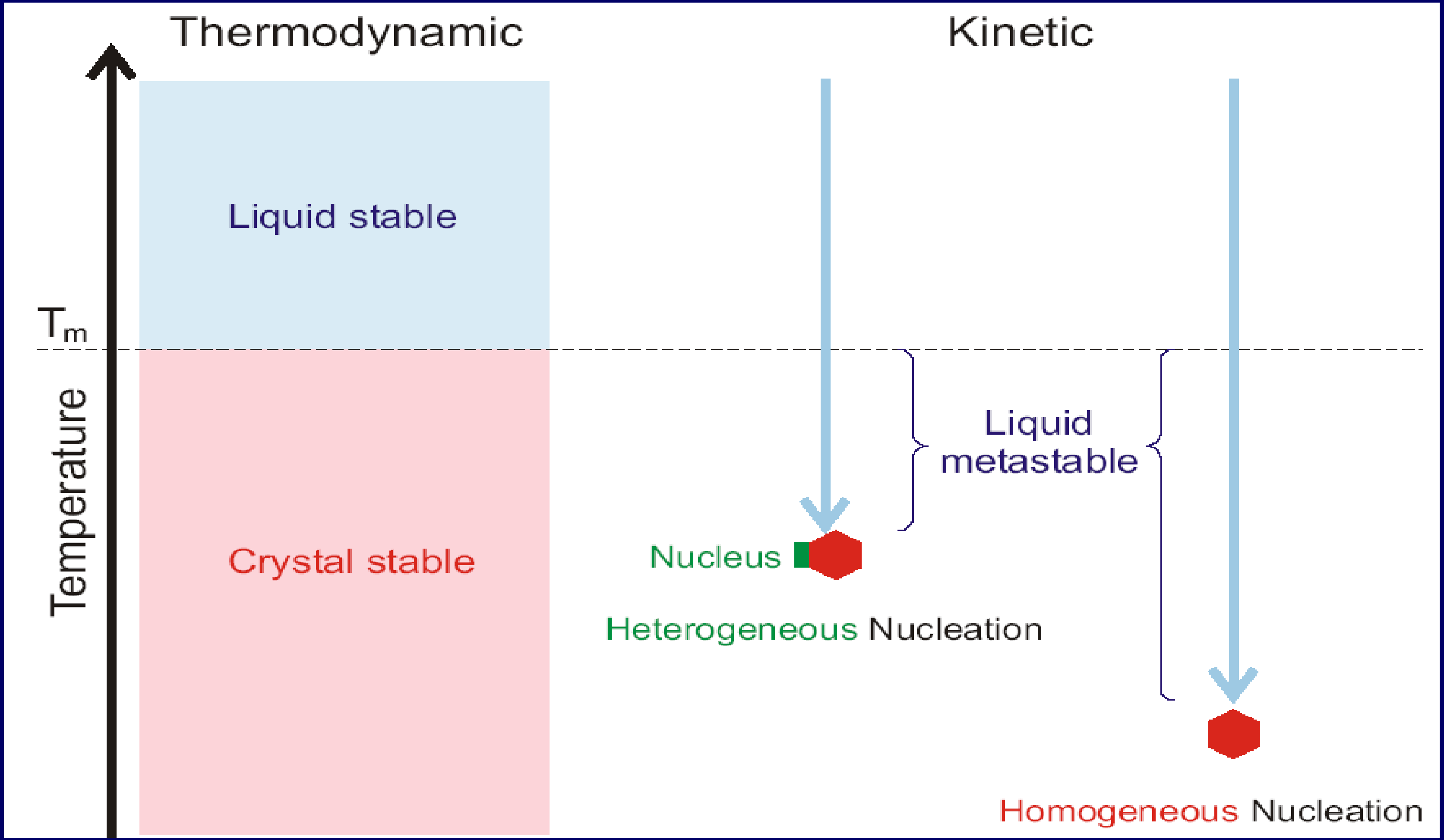
H$_2$O-trend, frost-point hygrometers above Colorado 1979-99 (courtesy Sam Oltmans)

Important effects:

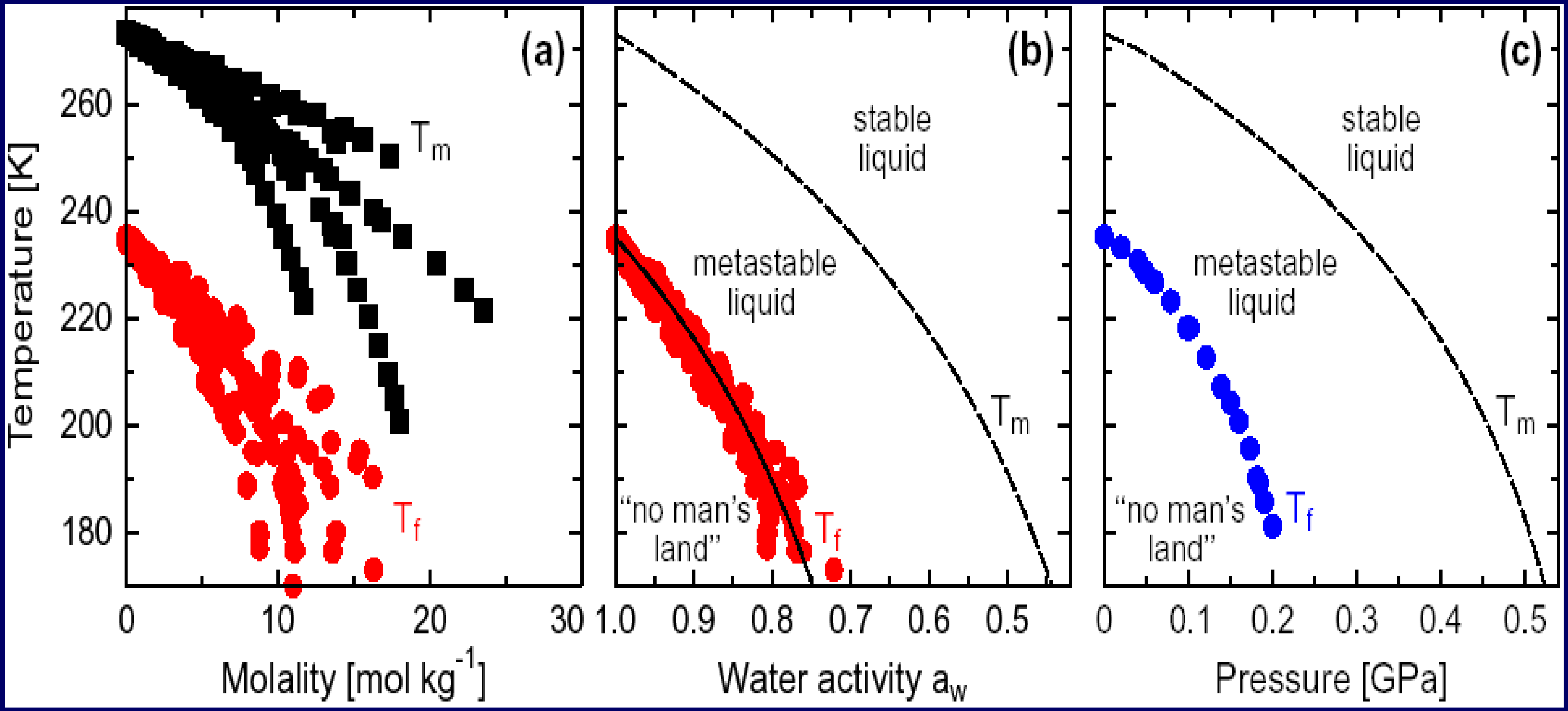
- ➔ Stratosphere cools
- ➔ Stratospheric HO_x chemistry enhanced


Supersatuation:
Decreasing tropical cloudiness?

"They live for a short time in very high clouds. In a pocket of motionlessness their temperature will drop to – 40ºC. They ought to freeze, but they don't."
Peter Høeg, *Miss Smilla's feeling for snow*

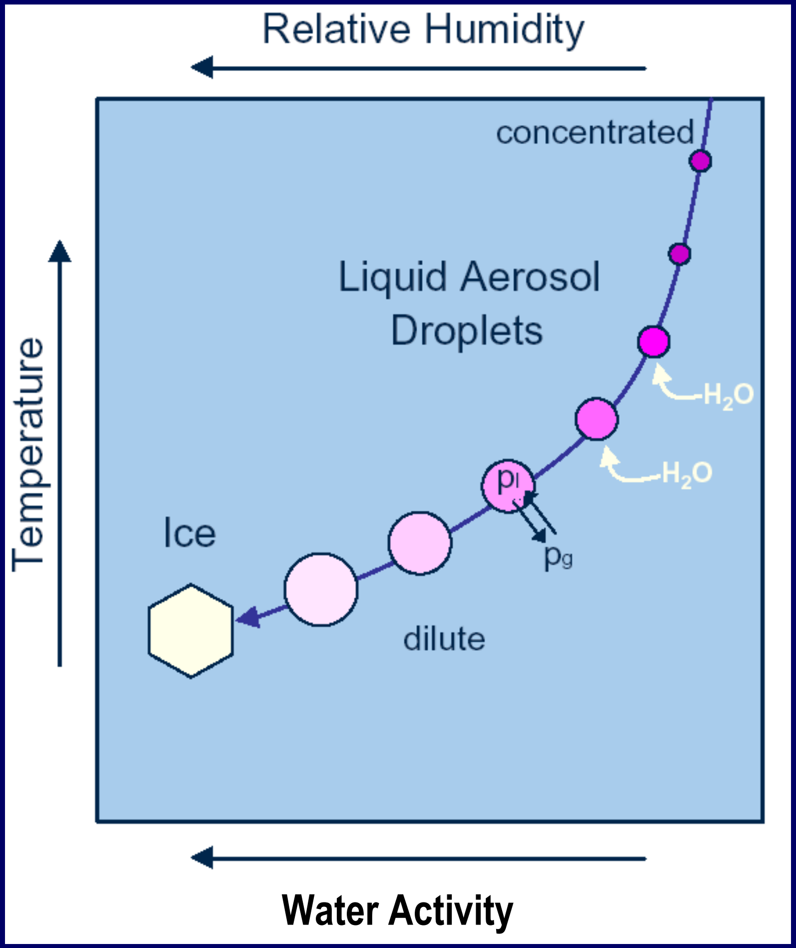


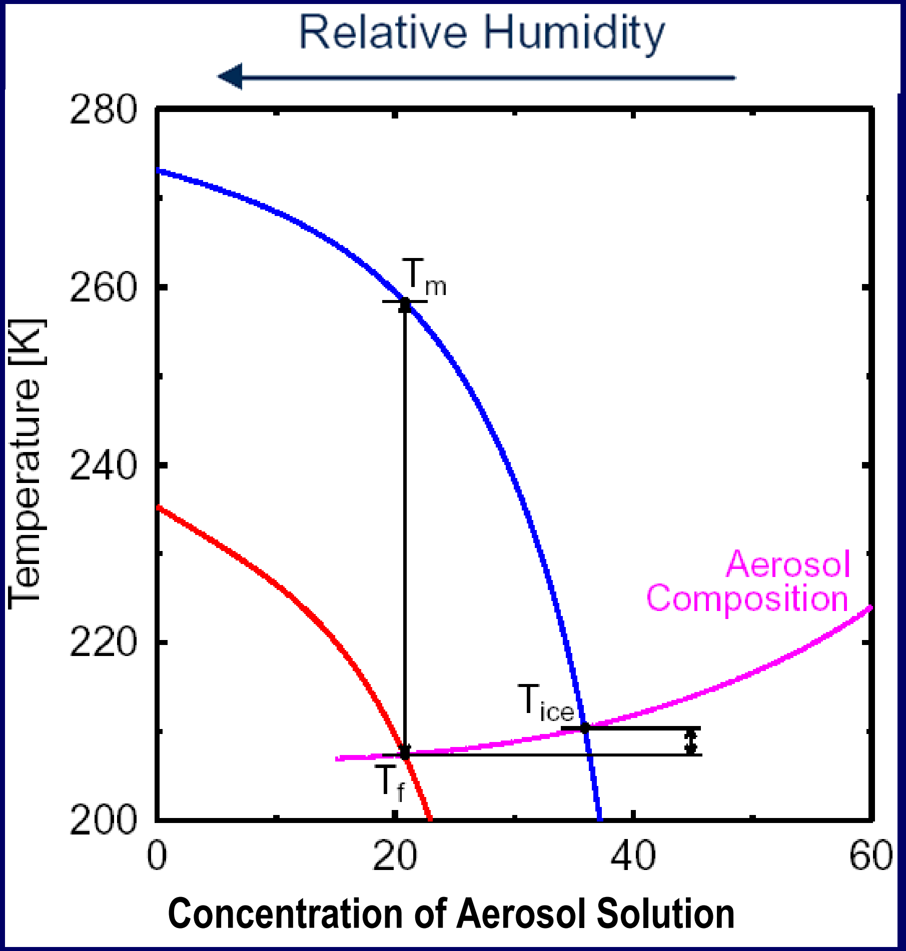
Water-activity-based ice nucleation theory



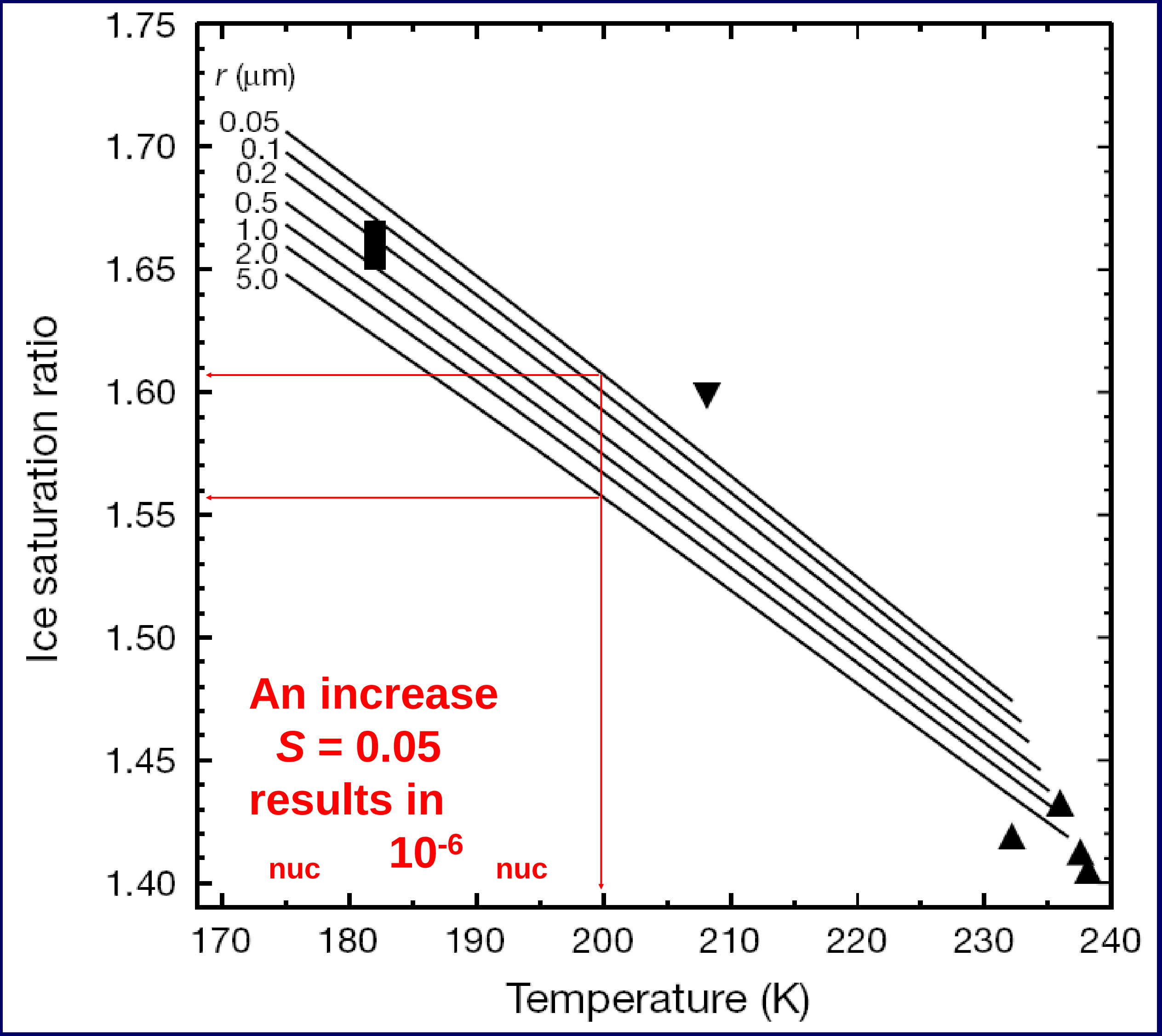
H_2SO_4	**HNO_3**	**HNO_3/H_2SO_4**
NH_4HSO_4	**$(NH_4)_2SO_4$**	**NH_4F**
LiCl	**NaCl**	**KCl**
NH_4Cl	**$CaCl_2$**	**$MnCl_2$**
$Ca(NO_3)_2$	**H_2O_2**	**urea**
ethylene	**glycol**	**glucose**

Atmospheric Application

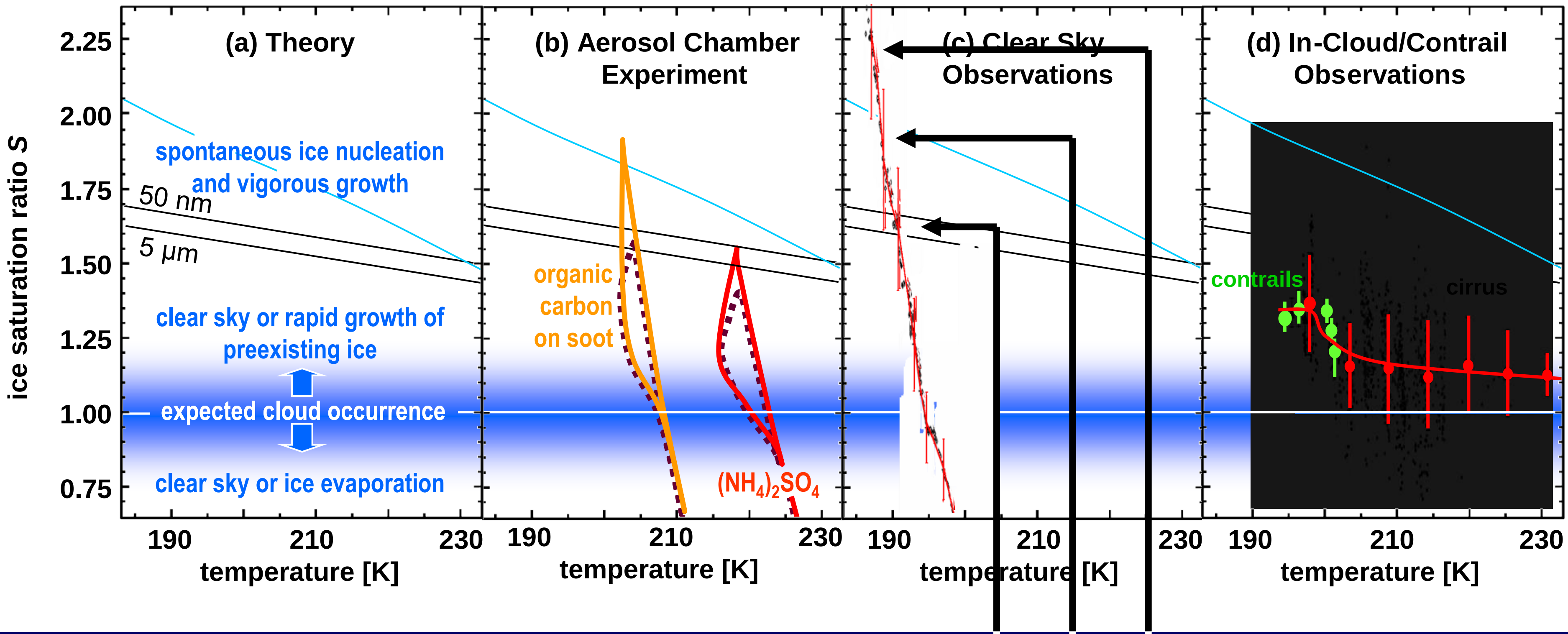




Dependence of nucleation rate on *S*



What does this mean for the observations?



nuc 1 min

nuc << 1 s

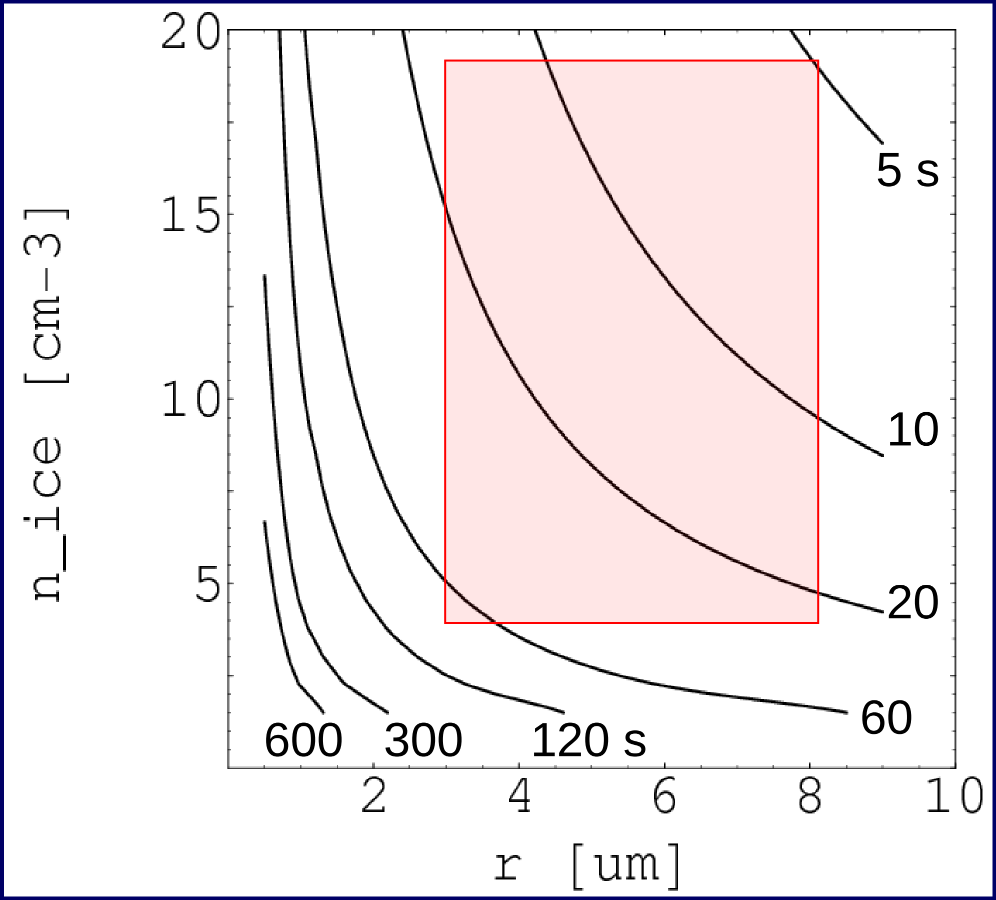
immediate

How does water vapor condense on ice particles?

$$\frac{dn_{H_2O}}{dt} = -4\pi\, D^* r\, n_{ice}\, (n_{H_2O} - n_{vap})$$

$$\tau_{cond} = \frac{1}{4\pi\, D^* r\, n_{ice}}$$

D^* modified diffusion constant including limitation by mass accomodation ( )



CRYSTAL-FACE

How does water vapor condense on ice particles?

$$\frac{dn_{H_2O}}{dt} = -4\pi D^* r\, n_{ice} \left(n_{H_2O} - n_{vap}\right)$$

$$\tau_{cond} = \frac{1}{4\pi D^* r\, n_{ice}}$$

How could supersaturation be maintained?

$$\frac{dn_{vap}}{dt} = \frac{dT}{dt}\frac{dn_{vap}}{dT} = -\Gamma w \frac{B}{T^2}\left(1 - T/B\right) n_{vap}$$

$$\tau_{cool} = \frac{1}{\Gamma w (B/T^2)\,(1 - T/B)}$$

$$\frac{dn_{\mathrm{H_2O}}}{dt} = \quad \ldots$$

$$\frac{dn_{\mathrm{vap}}}{dt} = \quad \ldots$$

How does water vapor condense on iceparticles?

$$\frac{dS}{dt} = \frac{d}{dt}\frac{n_{\mathrm{H_2O}}}{n_{\mathrm{vap}}}$$

$$= -\frac{S-1}{\tau_{cond}} + \frac{S}{\tau_{cool}} + \frac{S^0 - S}{\tau_{sed}} \geq 0$$

$$\tau_{cond} = \frac{1}{4\pi D^* r\, n_{\mathrm{ice}}}, \quad \tau_{cool} = \frac{1}{\Gamma w (B/T^2)(1 - T/B)}, \quad \tau_{sed} = \frac{\Delta z}{v_{sed}}$$

Steady-state S to a good approximation

$$\frac{dS}{dt} = -\frac{S-1}{\tau_{cond}} + \frac{S}{\tau_{cool}} + \frac{S^0 - S}{\tau_{sed}} \geq 0$$

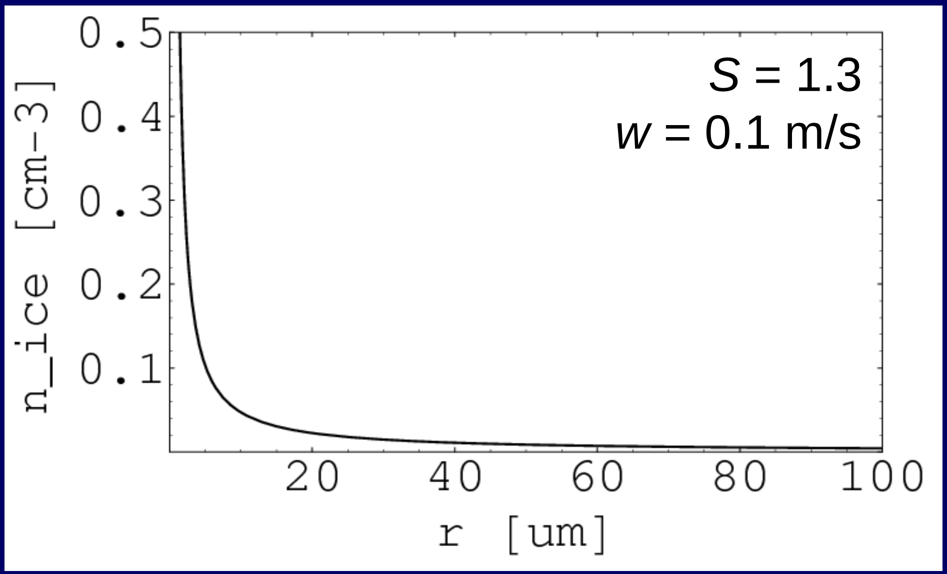
$$S - 1 \approx \frac{S\,\hat{w}}{\hat{r}\,\hat{n}_{\mathrm{ice}}}$$

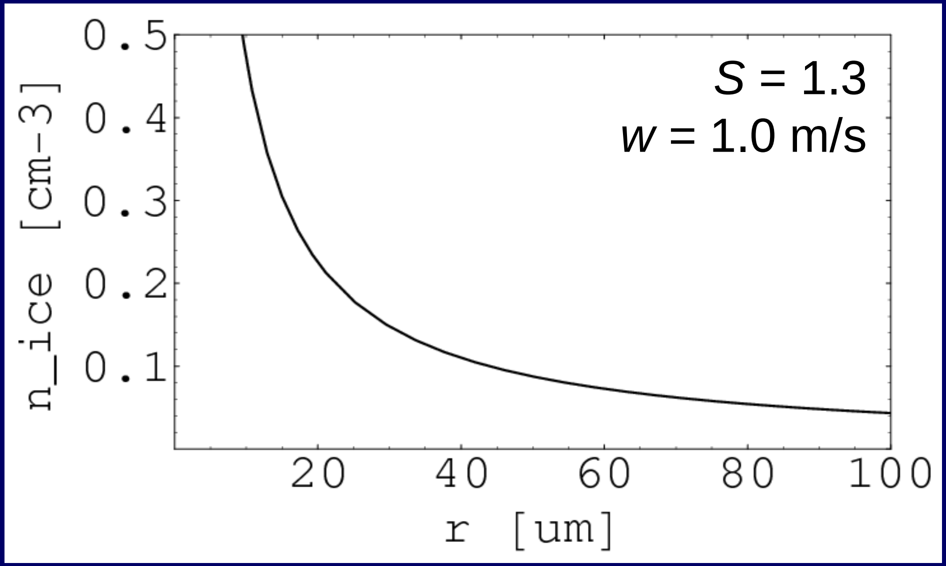
$$\hat{w} = w\,/\,(1\ \mathrm{m/s})$$

$$\hat{r} = r\,/\,(1\ \mu\mathrm{m})$$

$$\hat{n}_{\mathrm{ice}} = n_{\mathrm{ice}}\,/\,(1\ \mathrm{cm}^{-3})$$

Steady-state *S* in cirrus: traditional microphysical understanding



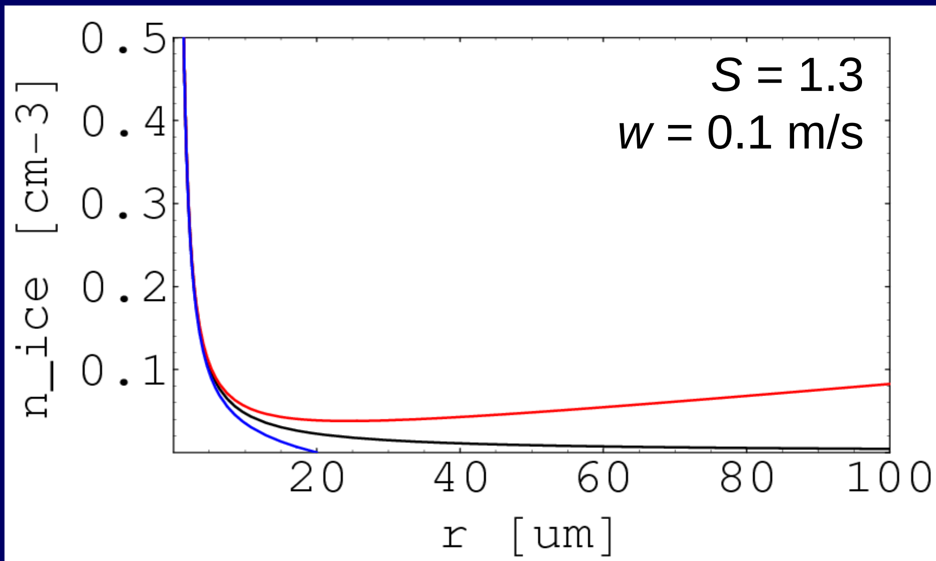


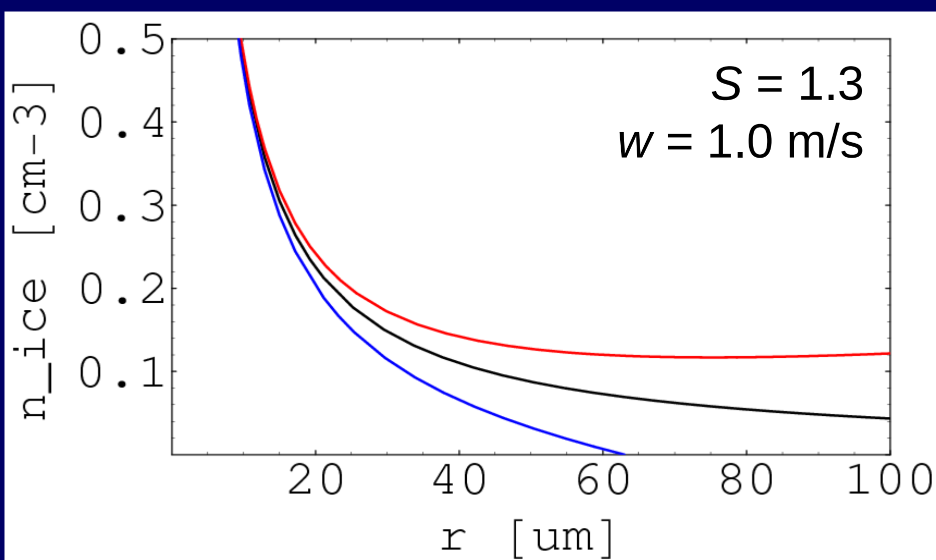
Low number-density cirrus:

Equilibrium curves for steady-state S = 1.3.

p = 100 hPa
T = 200 K
= 1
S^0 = 1.6

Steady-state *S* in cirrus: traditional microphysical understanding





Low number-density cirrus:

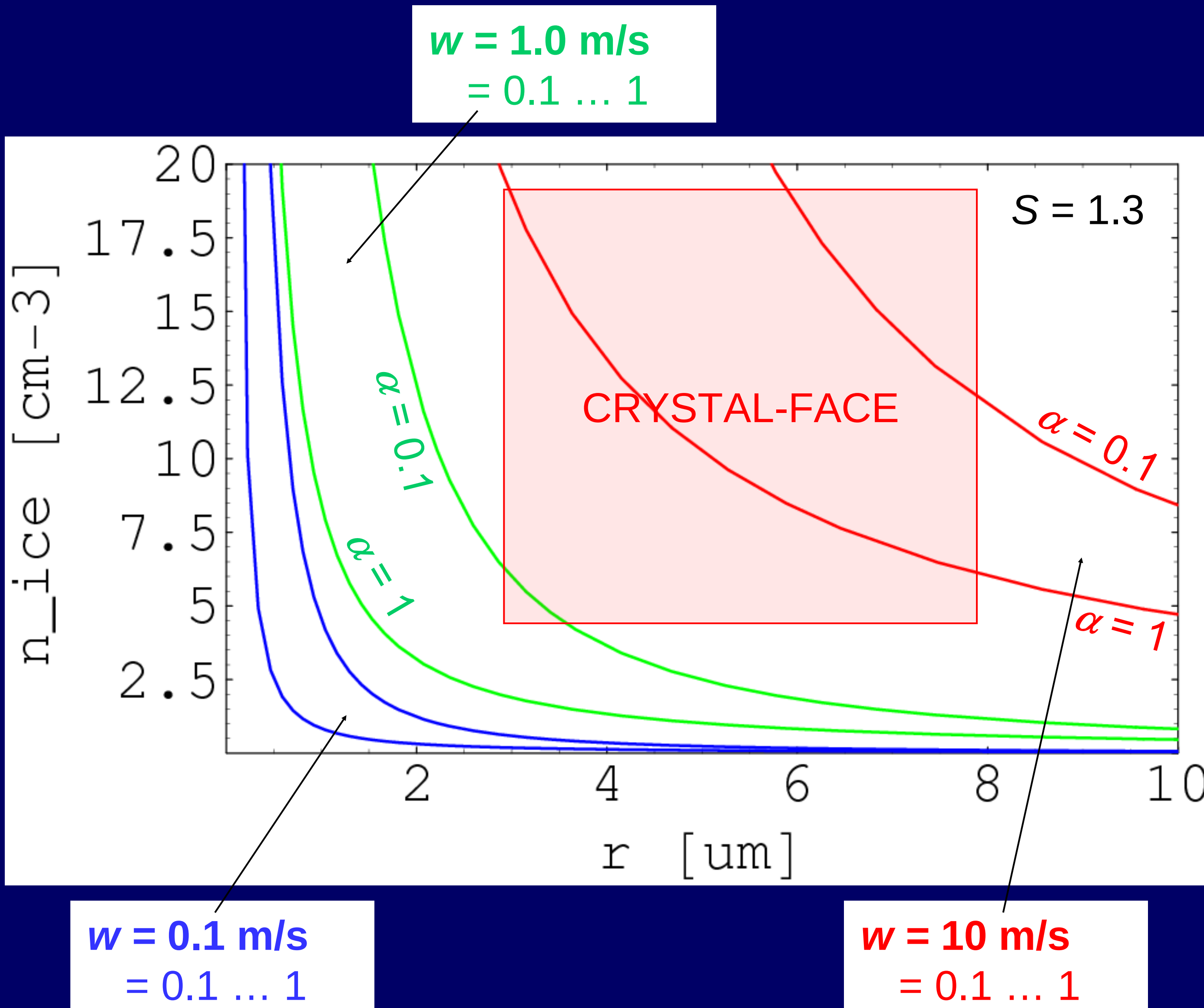
Equilibrium curves for steady-state $S = 1.3$.

$p = 100$ hPa
$T = 200$ K
= 1
$S^0 = 1.6$

Including sedimentation in a layer of thickness:

z = 100 m
z = 1000 m

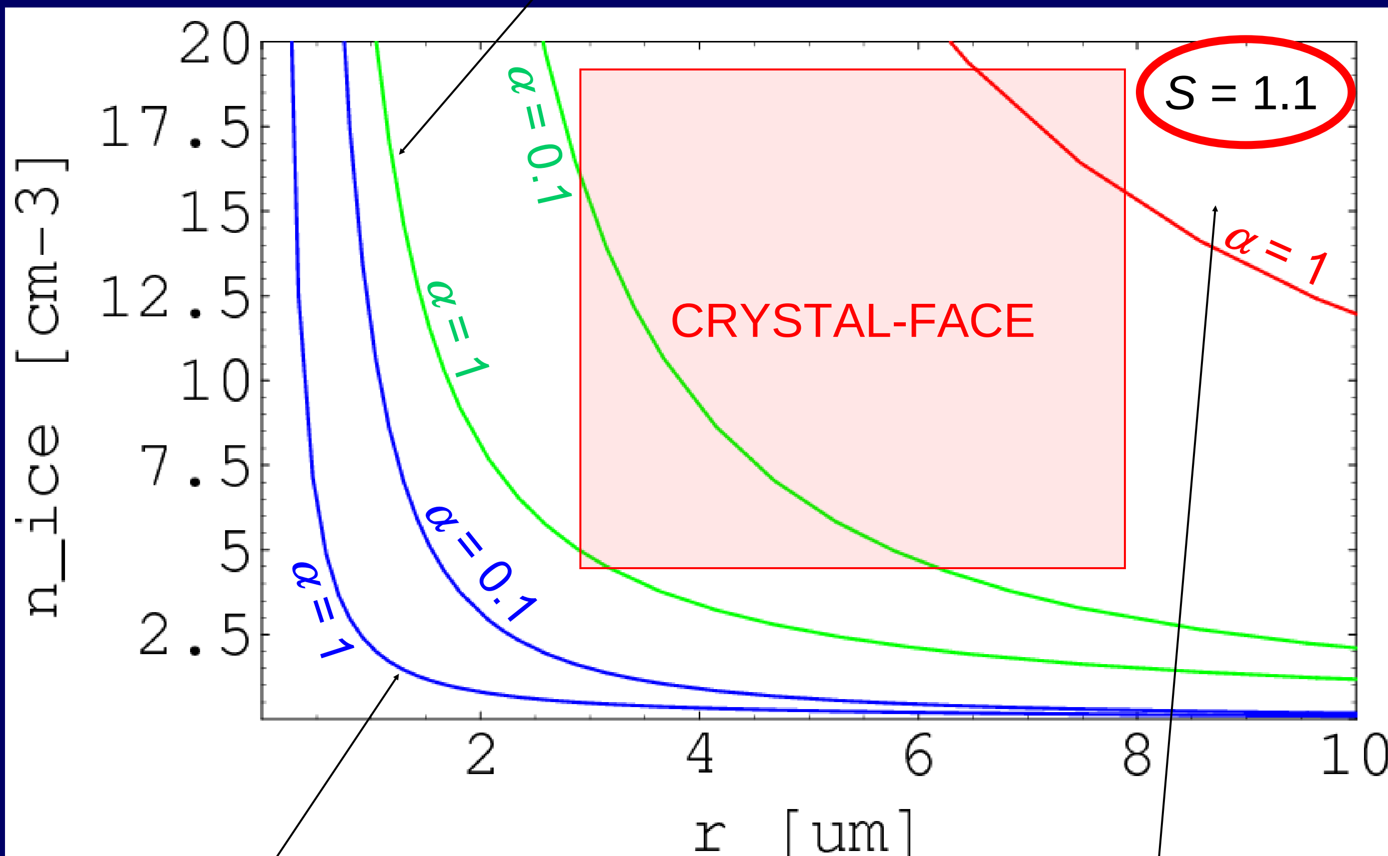
Steady-state *S* in cirrus: traditional microphysical understanding



CRYSTAL-FACE data could be explained assuming strong updrafts and low mass accommo-dation

Steady-state *S* in cirrus: traditional microphysical understanding

w = 1.0 m/s
= 0.1 … 1



w = 0.1 m/s
= 0.1 … 1

w = 10 m/s
= 0.1 … 1

CRYSTAL-FACE data could be explained assuming strong updrafts and low mass accommo-dation

Explanations??? Hypotheses??? Speculations???

→ **How good are the data?**

→ **Potential out-of-cloud effects:**

Lack of preexisting aerosol?

Underestimated vapor pressure of supercooled water?

Surface nucleation?

→ **Potential in-cloud effects:**

Control by ice nuclei?

Mesoscale temperature fluctuations?

Subresolution patchiness?

HNO_3 deposition on ice, forming NAT?

Intrinsic limitations on growth of ice?

Cubic ice?

Overpopulated tail of high velocity molecules?

Several slides with unpublished data removed here

New results from Pre-AVE campaign

Aircraft-balloon intercomparisons

European measurements from Geophysica and the German Learjet

Conclusion: how good are the data?

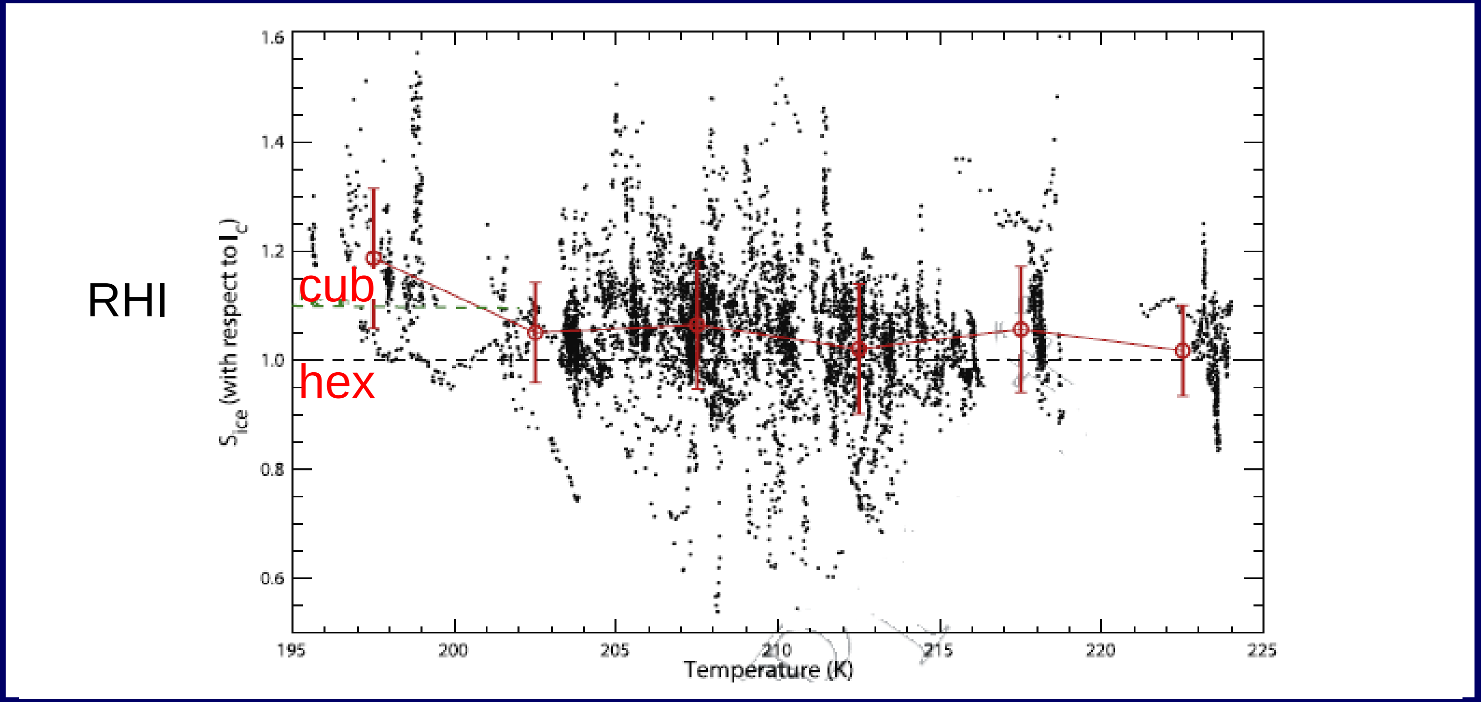
The balloon-borne RHI are significantly lower than the aircraft-borne RHI = *S*.

The aircraft-borne data show significant discrepancies with respect to each other.

However, all data sets show large $S - 1$, exceeding the homogeneous freezing limit and – at times – even exceeding pure liquid water saturation.

All data show significant persistent $S - 1 >> 0$ inside clouds.

Shilling et al., Vapor Pressure of Cubic Ice, GRL 2006



Gao et al.; Harvard water vapor instrument
Shilling et al.: JPL tunable diode laser hygrometer

> sublimation of crystals in the inlet of the HWV can result in anomalously high H_2O

> include only measurements when $_{cond}$ < 3 minutes

> include only measurements when $w < 0.5$ m/s

Explanations??? Hypotheses??? Speculations???

→ **How good are the data?**

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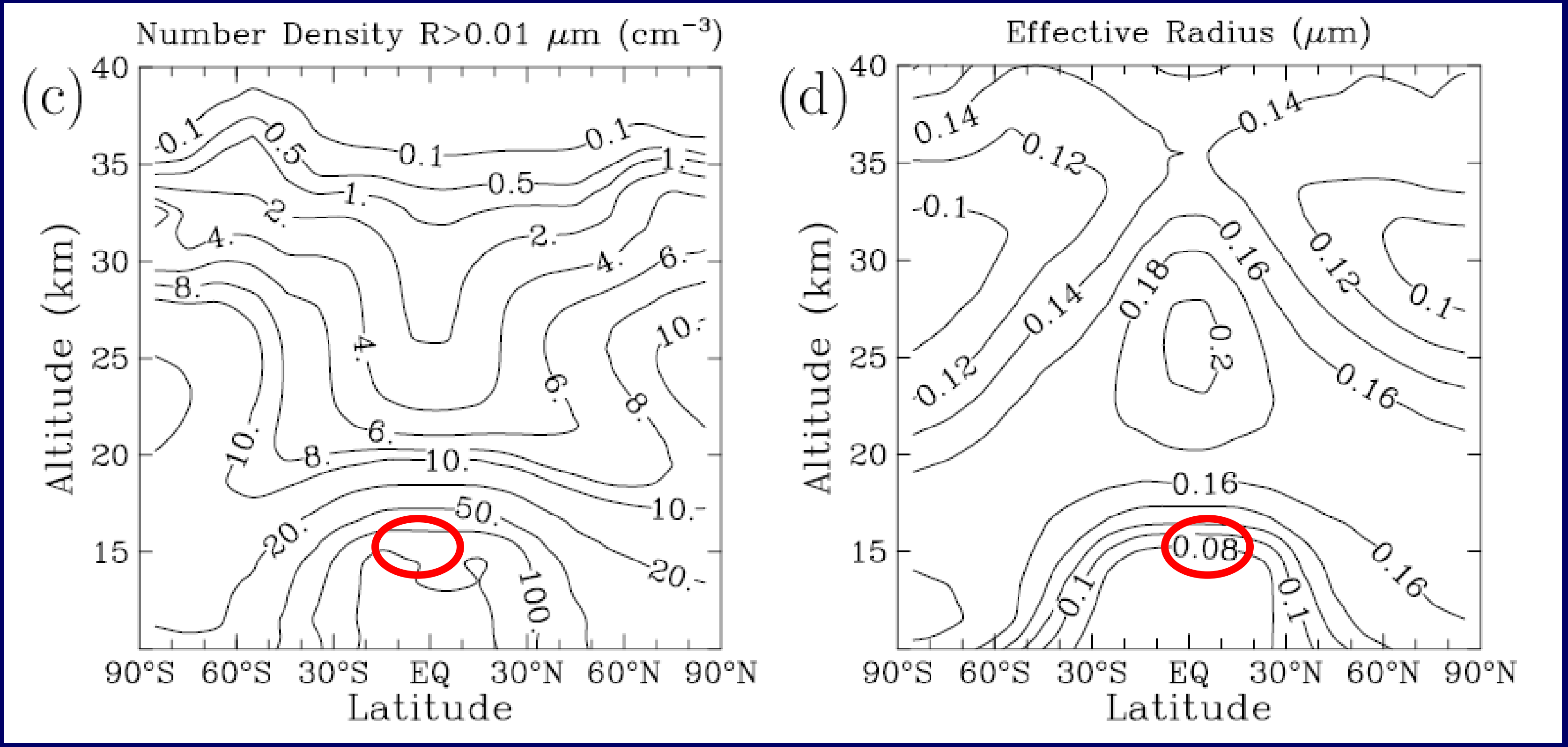
Lack of preexisting aerosol?



Jensen et al., 2005:

Measurements made during the descent:

log-normal aerosol size distribution

$n = 100$ cm^{-3}, $r_m = 0.025$ μm, = 1.4

Debra Weisenstein, 2-D aerosol model, from "Assessment of Stratospheric Aerosol Properties", SPARC Report

Potential out-of-cloud effects:

Underestimated vapor pressure of supercooled water?

Outside ice clouds the determination of the relative humidity at which ice nucleation occurs depends also on the saturation vapor pressure of supercooled water, which has to be extrapolated for use below 230 K (*8*), possibly leading to errors up to 20 %.

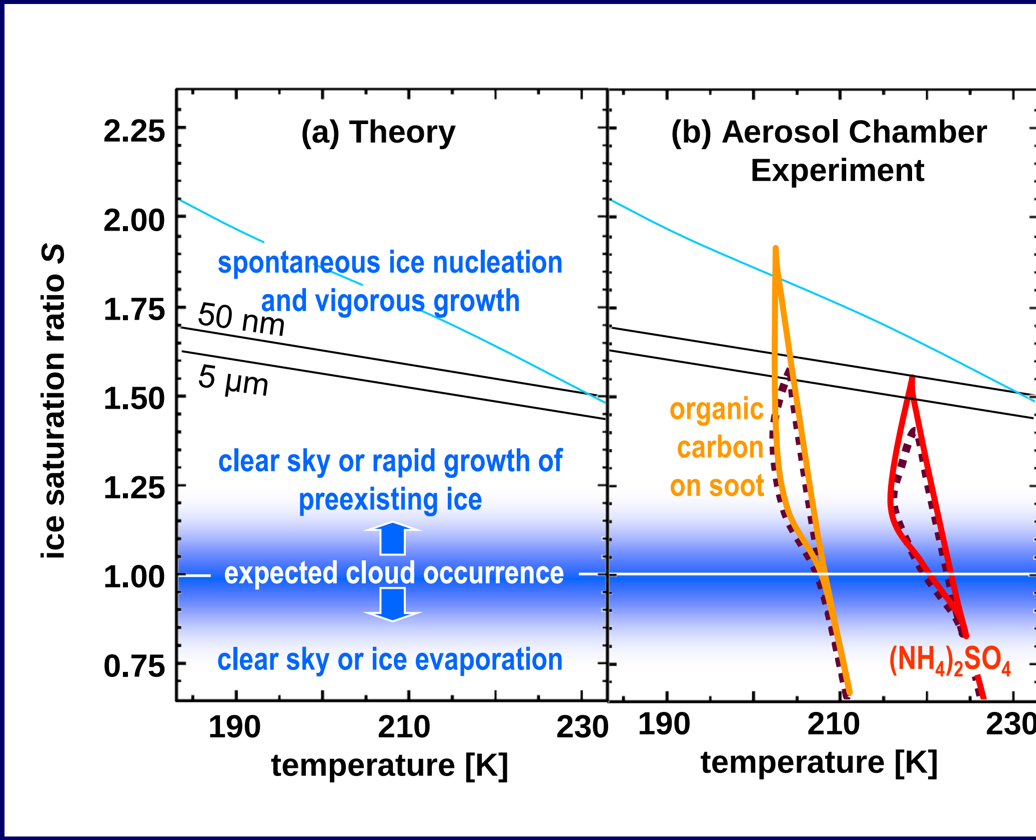
However, if the error was really that large, should it not have been caught in laboratory experiments?

Potential out-of-cloud effects:

Surface nucleation?

If water-rich aerosols are covered by organic surfactants, nucleation might be suppressed if it starts at the surface (A. Tabazadeh and coworkers).

But evidence for surface nucleation is controversial. Furthermore, it is not known how likely complete coverage by organics on the aerosols is.



Potential in-cloud effects:

Control by ice nuclei?

The presence of heterogeneous ice nuclei in cloud-free air may initiate ice nucleation below the homogeneous nucleation threshold, leading to clouds with low ice particle number densities, in which supersaturations might be sustained for relatively long periods.

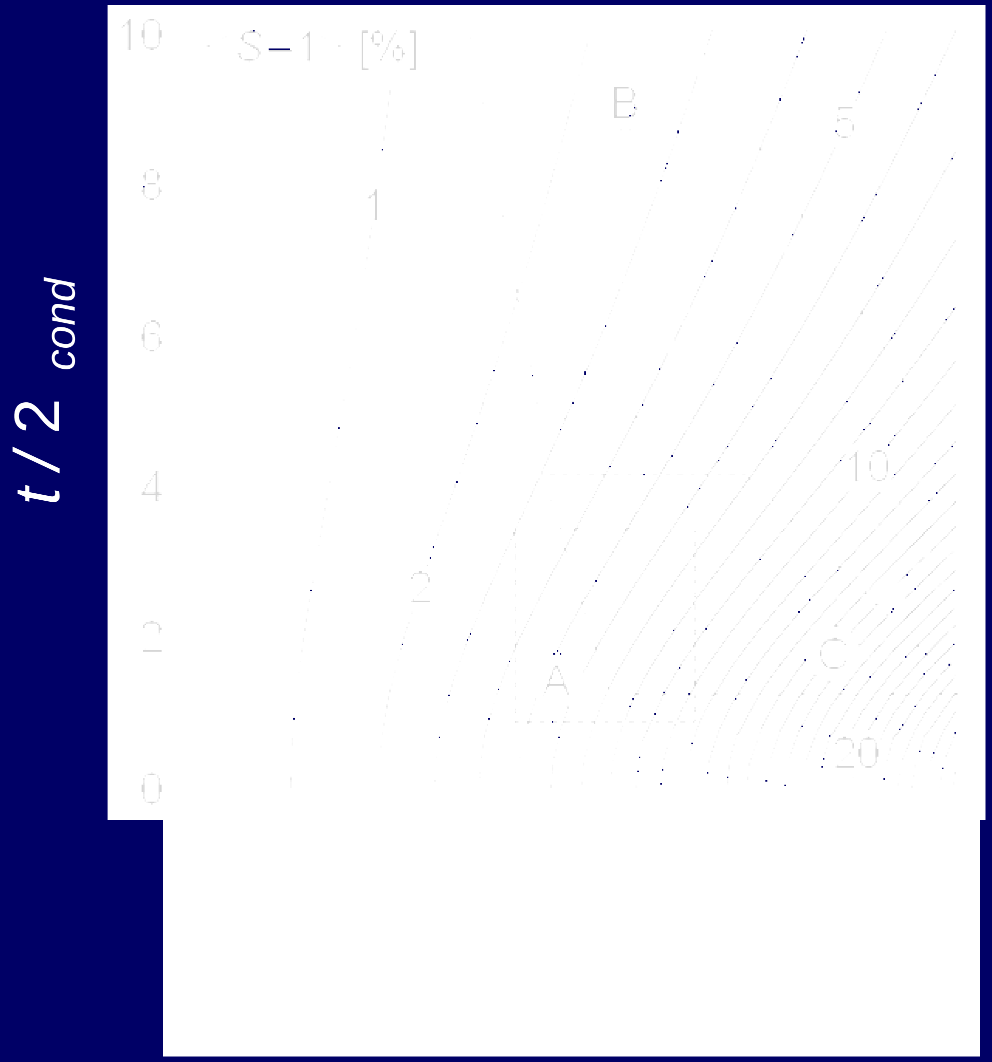
… but how can this provide a persistent effect?

Potential in-cloud effects:

Mesoscale temperature fluctuations?

T oscillations – due to the nonlinearity of the Clausius-Clapeyron equation – may cause *average* supersaturations.

… but average is not persistent, and the effect is moderate.



Campaigns:

A SUCCESS

B CRYSTAL-FACE

C SESAME PSC

Potential in-cloud effects:

Subresolution patchyness?

Cirrocumulus undulatus, 15 Sept 2006 above Zürich

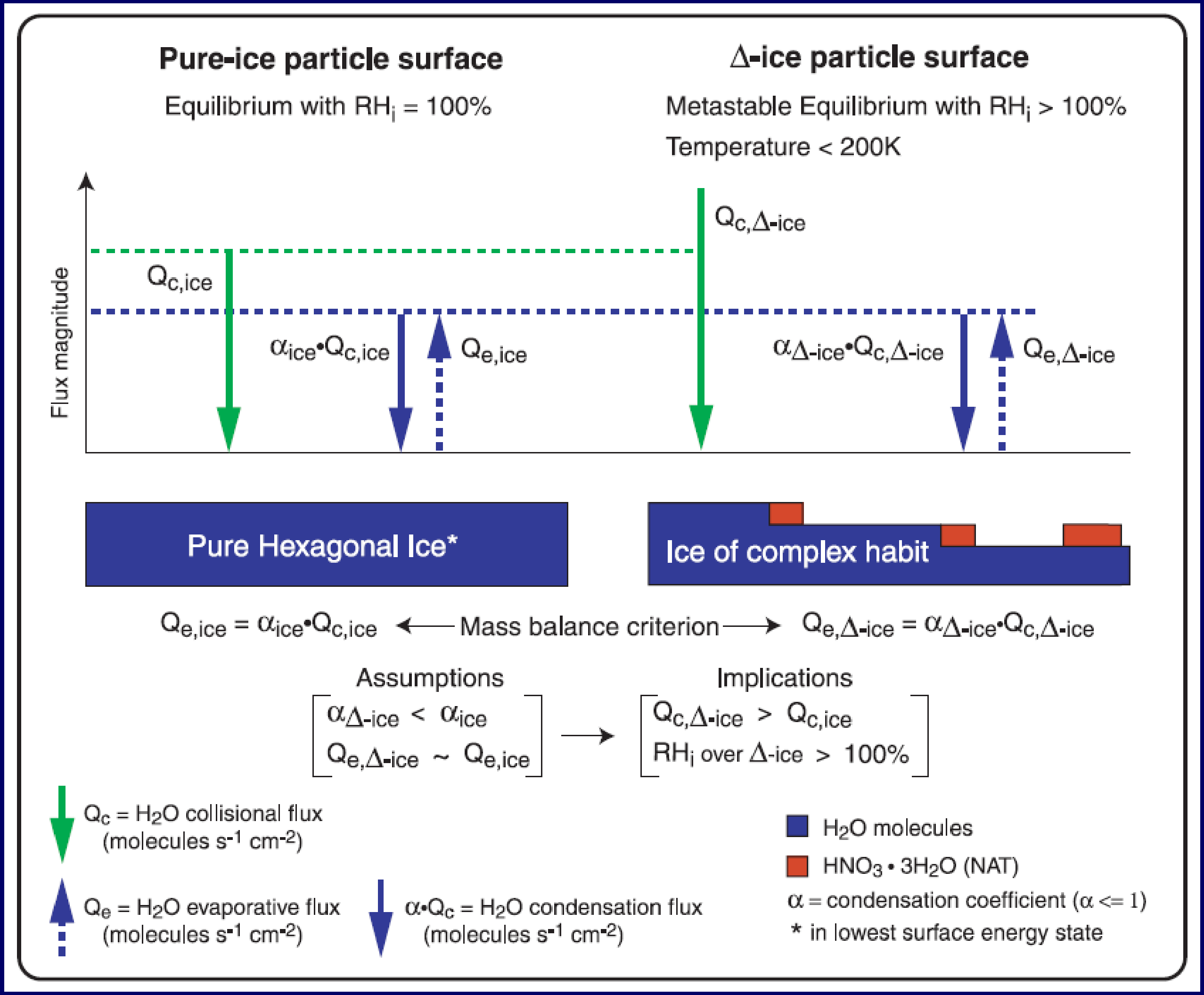
Potential in-cloud effects:

HNO_3 deposition on ice, forming NAT?

From Gao et al., Science 2004

Blocking of growth sites?

But no lab evidence!.



Potential in-cloud effects:

Intrinsic limitations on growth of ice?

Pratte et al., The Kinetics of H_2O Vapor Condensation and Evaporation on Different Types of Ice in the Range 130-210 K, JPC, 2006

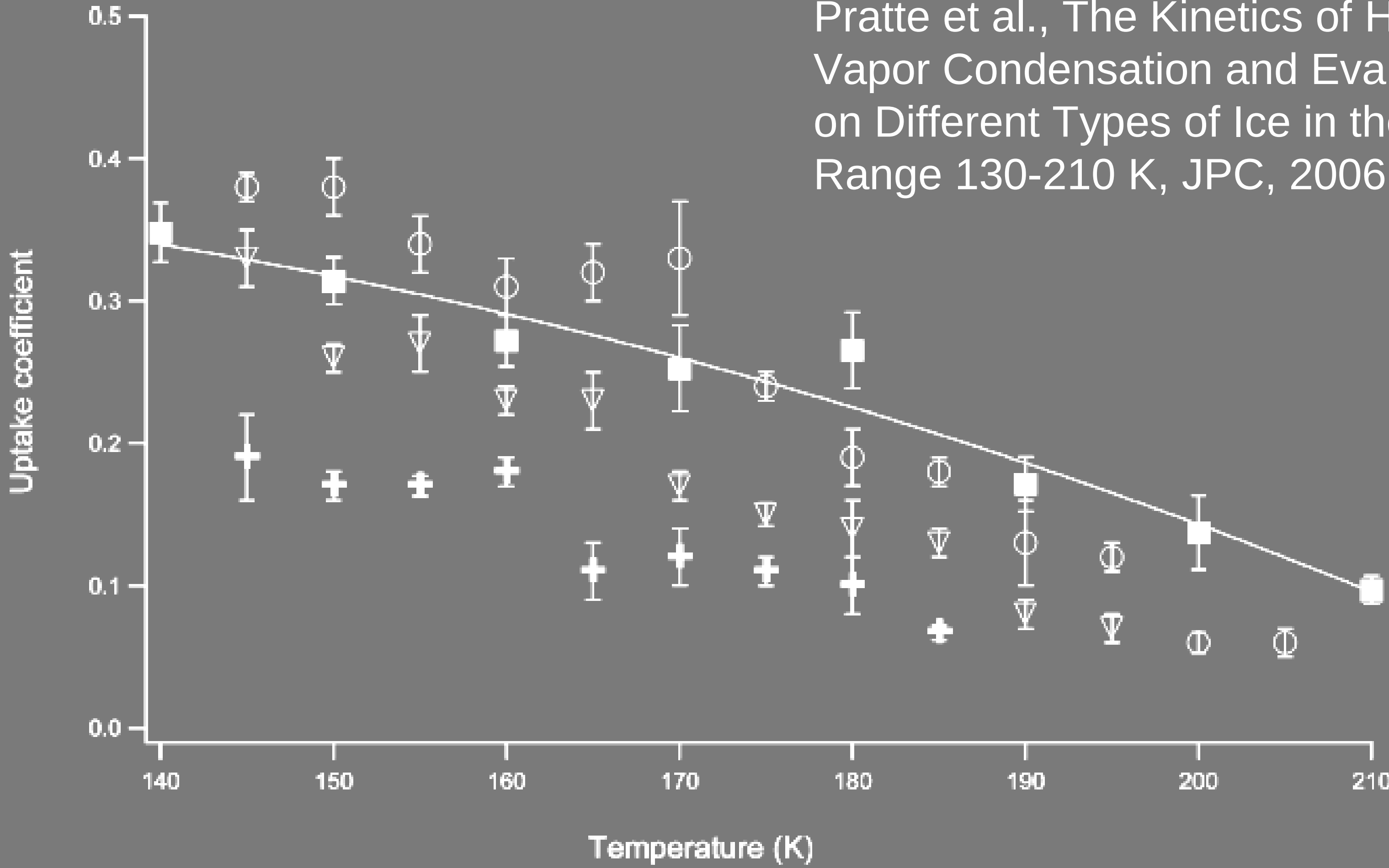


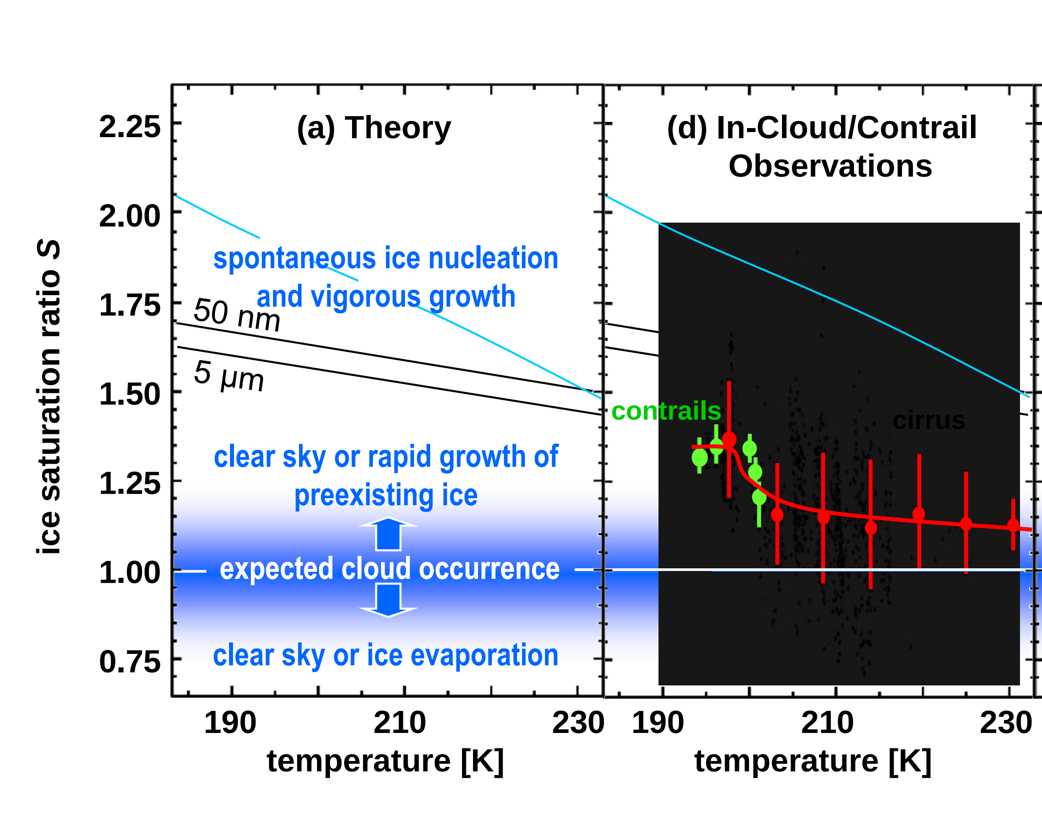
Figure 4. Uptake coefficient γ for SC ice plotted as a function of temperature for three different doses, namely, 1.0×10^{15} (+), 9.0×10^{15} (▽), and 5.0×10^{16} (○) molecules/pulse. B ice (■) data are presented as a reference.

Potential in-cloud effects:

Cubic ice?

Recent laboratory studies have shown that below 200 K a metastable form of ice – cubic ice – nucleates first and might persist in clouds. The equilibrium vapor pressure for cubic ice is about 10 % higher than that over stable hexagonal ice.

But unlikely higher!



Potential in-cloud effects:

Overpopulated tail of high velocity molecules?

Molecular velocity distributions and generalized scale invariance in the turbulent atmosphere

Tuck et al., Faraday Discuss., 2005

An overpopulated tail of high velocity molecules in atmospheric probability distribution functions will also affect the access of condensable vapours to particle surfaces, particularly in the case of water, which as a relatively light molecule may be expected to show a relatively high overpopulation of translationally hot molecules. Calculations of vapour flux to ice crystals, for example in polar stratospheric clouds or high cirrus near the tropical tropopause, could incur substantial error by using traditional x^2 2 Dt formulations of molecular diffusion.

… *however, isn't this contradicting laboratory evidence?*

Summary of Potential Explanations:

Data quality:

There are significant discrepancies whose origin needs to be investigated!

However, there is little doubt that the observed S cannot be explained on the basis of traditional microphysics!

Potential out-of-cloud effects:

Lack of preexisting aerosol?

But air masses would need to be almost void of aqueous aerosols.

Underestimated vapor pressure of supercooled water?

But the required > 20 % error is not supported by laboratory evidence.

Surface nucleation?

If ice nucleated at aerosol surface and the surface was completely covered by organics …

Summary of Potential Explanations:

Potential in-cloud effects:

Control by ice nuclei?

Ice nuclei might suppress homogeneous nucleation, but it remains unclear how this can lead to persistent $S > 1$.

Mesoscale temperature fluctuations?

Due to the nonlinearity of the Clausius-Clapeyron relation, fluctuations cause an average, but not the observed continuous supersaturation.

Subresolution patchiness?

Ice patchiness may cause apparent in-cloud supersaturation, but a verification will have to await higher resolution instrumentation.

HNO_3 deposition on ice, forming NAT?

Nitric acid trihydrate (NAT) blocking growth sites on the ice, but laboratory investigations of this effect are not clarifying the issue.

Intrinsic limitations on growth of ice?

Recent lab studies suggest impeded growth due to low H_2O mass accommodation, but how can the resulting S be as persistent?

Cubic ice?

Lab studies show that cubic ice forms as a transient at temperatures below 190 K, but this cannot explain $S > 1.1$.

Overpopulated tail of high velocity molecules?

Translationally hot water molecules could reduce the access of con-densable vapor to particle surfaces, but w/o experimental evidence.

Summary of Potential Explanations:

The way forward?

Suggestion:

Dedicated workshop: involved instrumentalists, key lab people, key cloud/aerosol modellers and ice theoreticians!

Dedicated instrument intercomparisons, e.g. in a cloud chamber!

Dedicated lab investigations on impurities on ice!