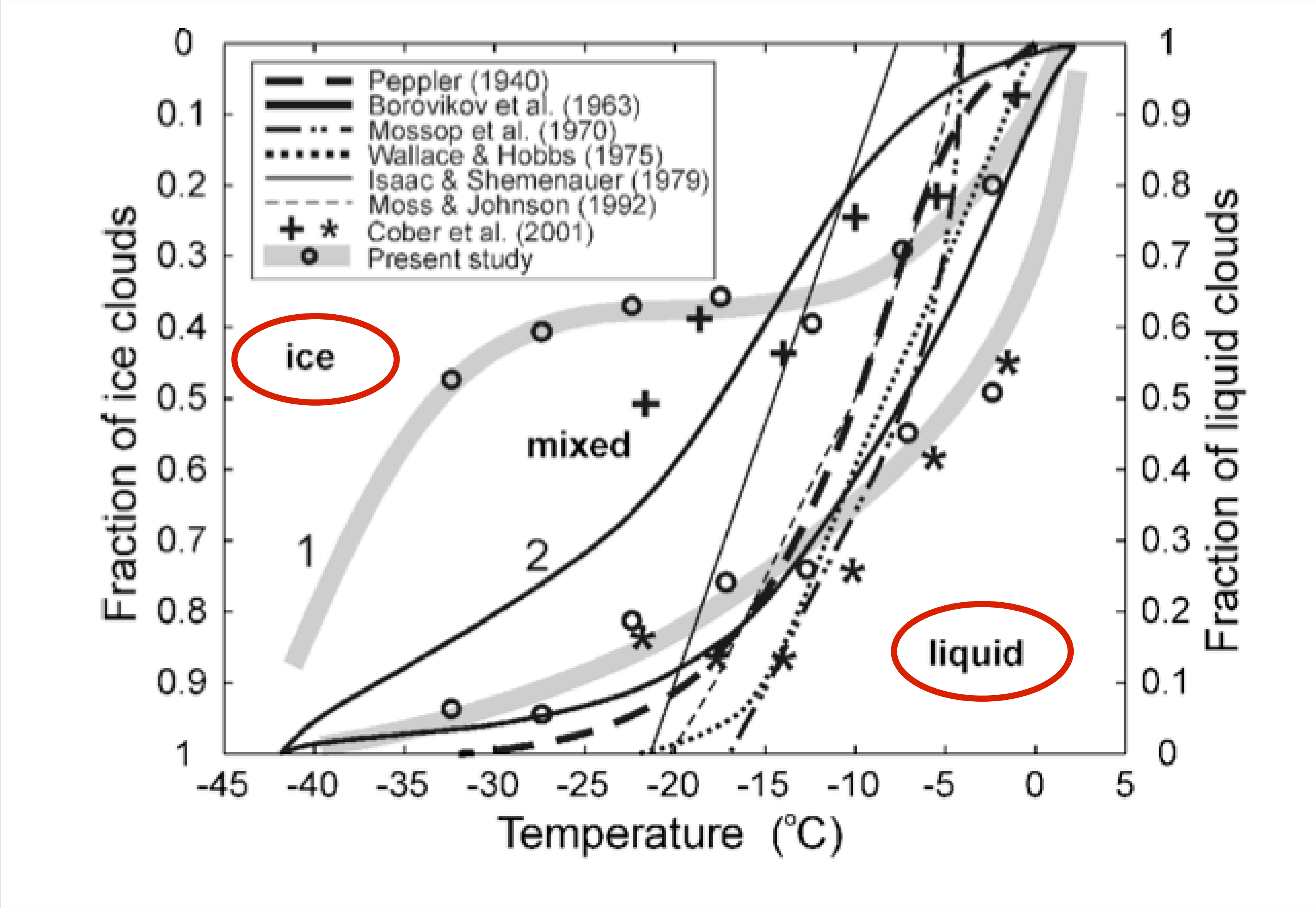
# A 30-minute flight segment and a 3-day lab experiment

asking questions about ice formation
in the atmosphere,
and
about the stochastic versus singular
character of heterogeneous ice nucleation

Gabor Vali

Talk given at the ICIS-07 Third International Workshop on Ice Nucleation
Karlsruhe, September 26, 2007

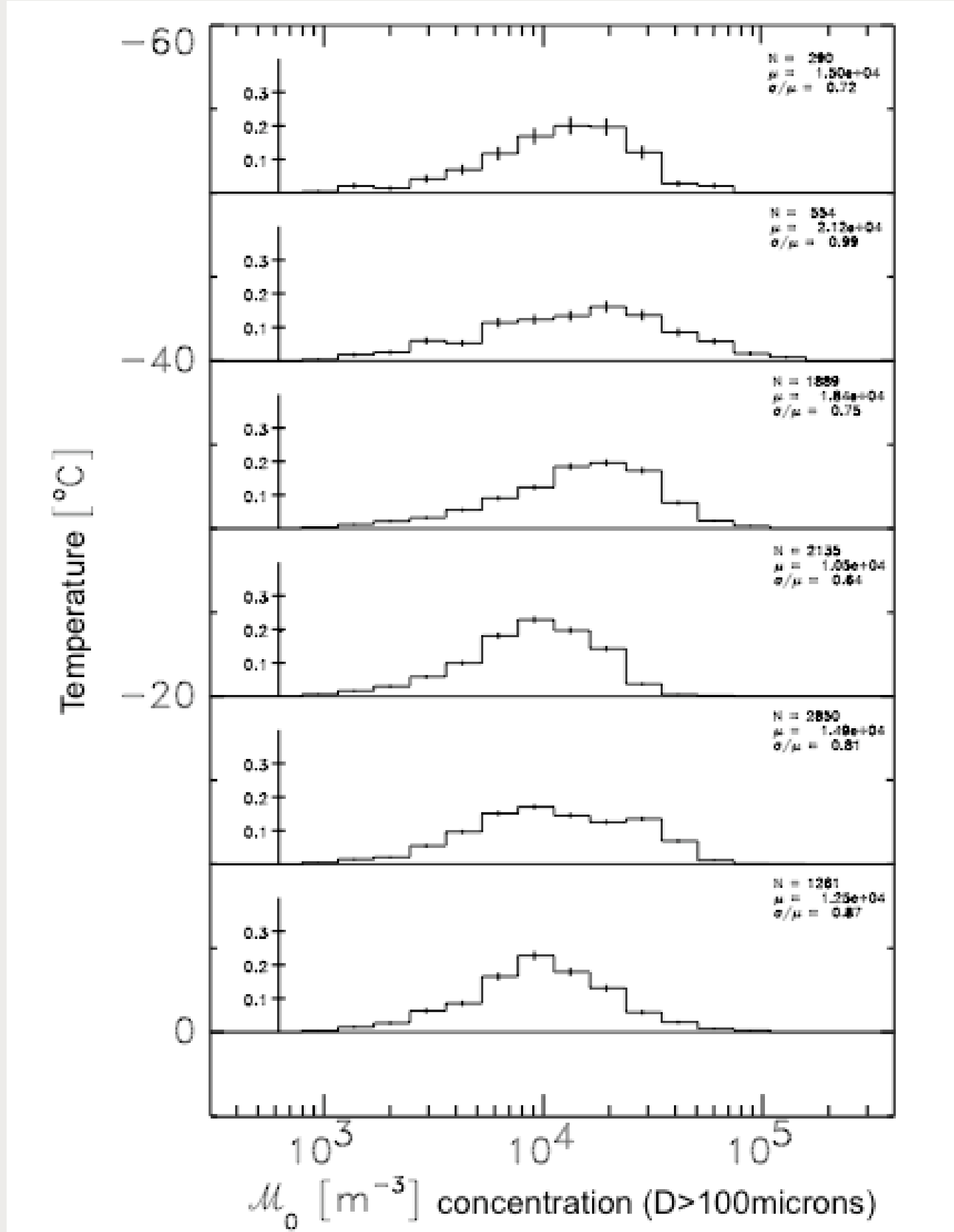
Source: Korolev et al., 2003 (Quart. J. Roy. Meteor. Soc.)



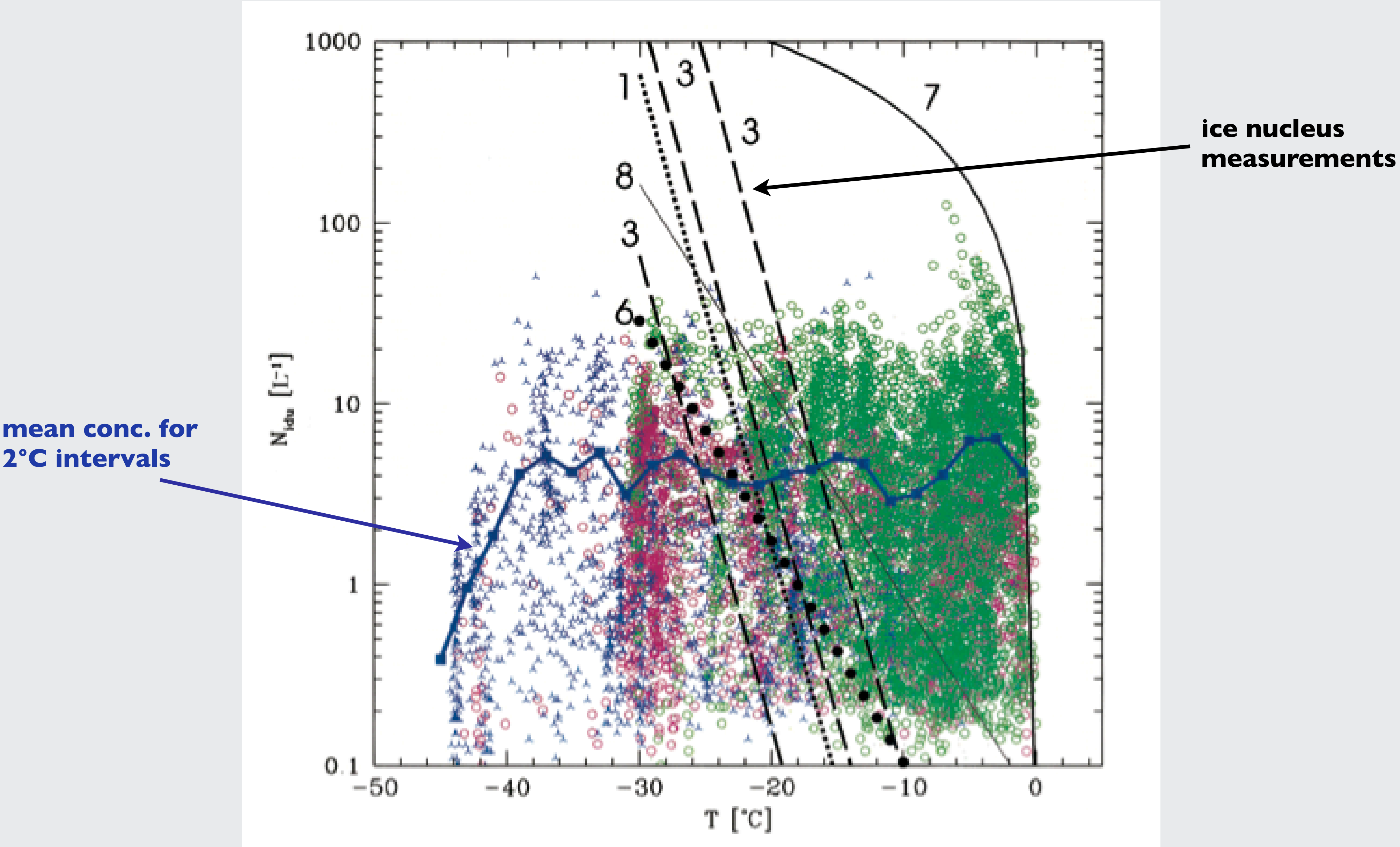

Zones of ice and liquid clouds by temperature.

Source: Field et al., 2005
(Quart. J. Roy. Meteor. Soc.

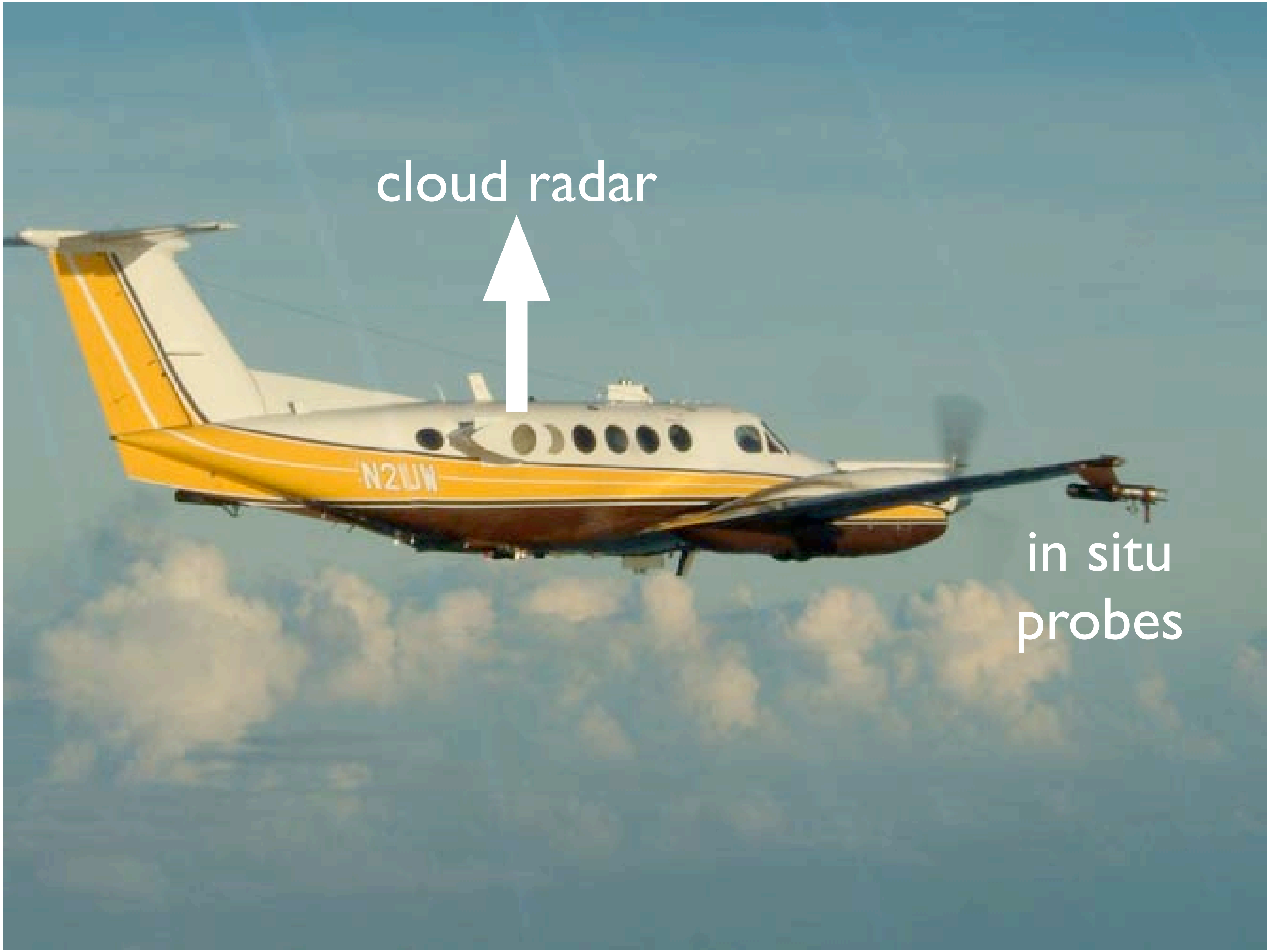
# Frequency distributions ice mass observed at different temperatures.



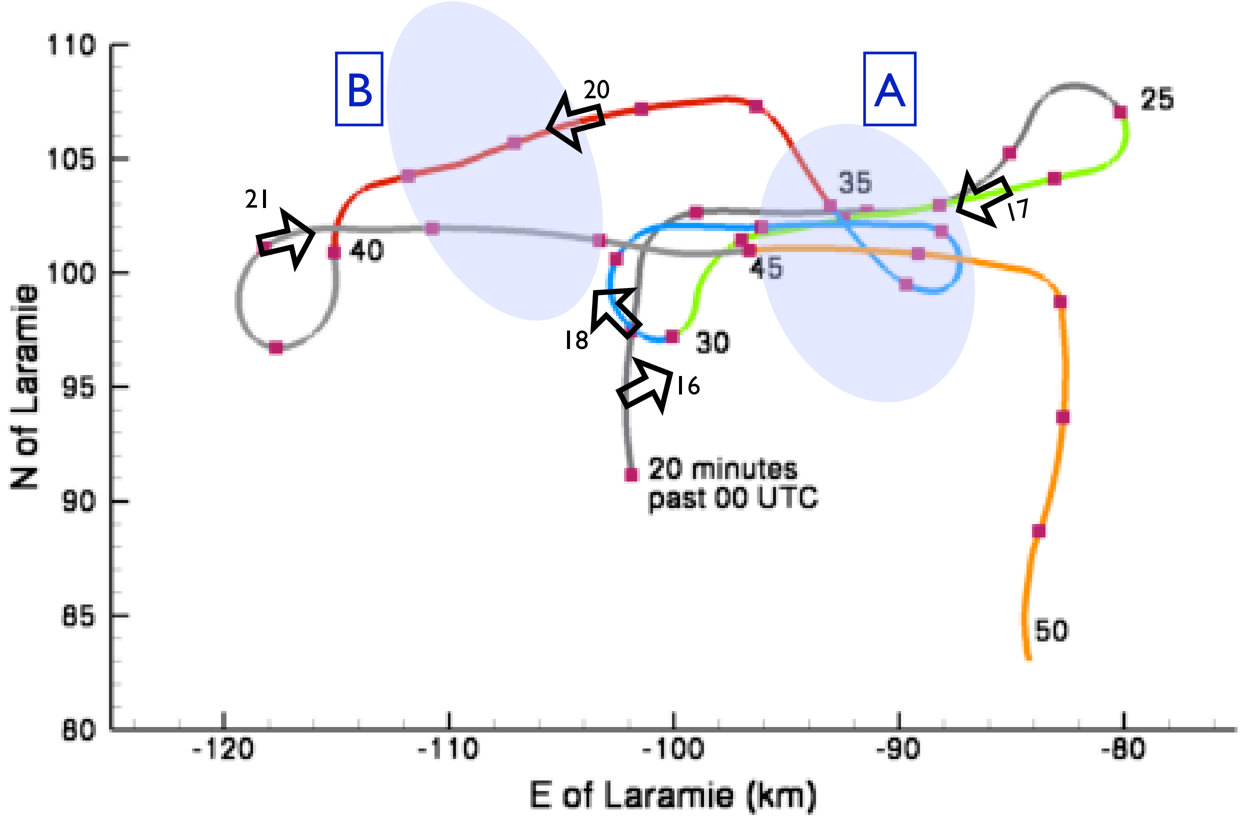
Source: Gultepe et al., 2001 (Int'l J. Climat.)

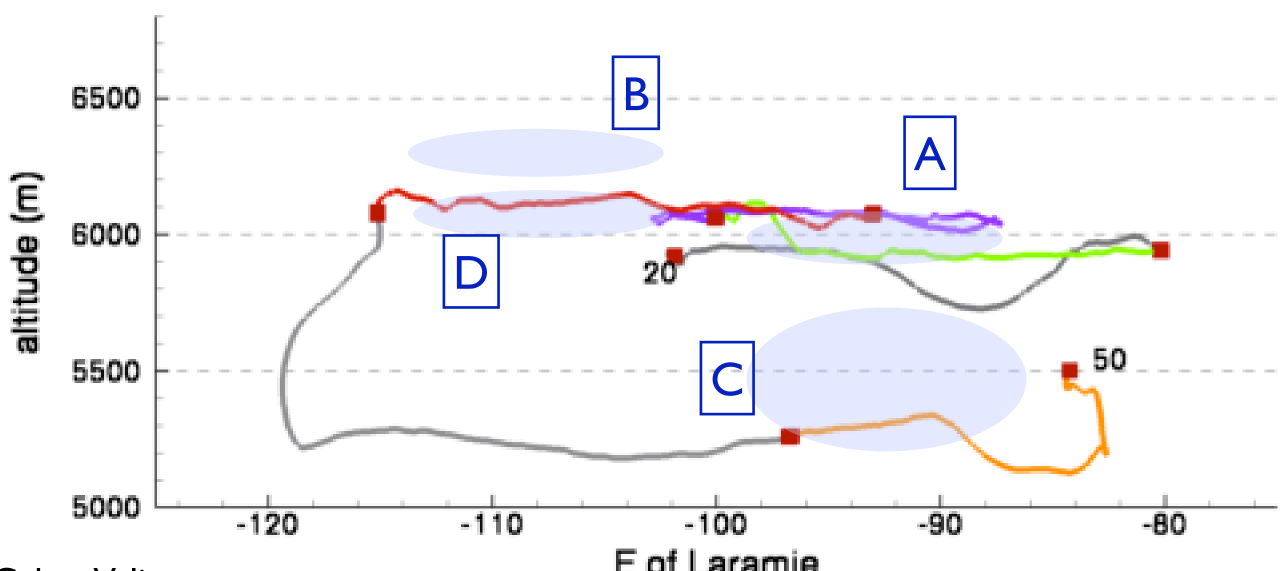



Ice particle concentrations from aircraft measurements (2D-C probe) in various projects

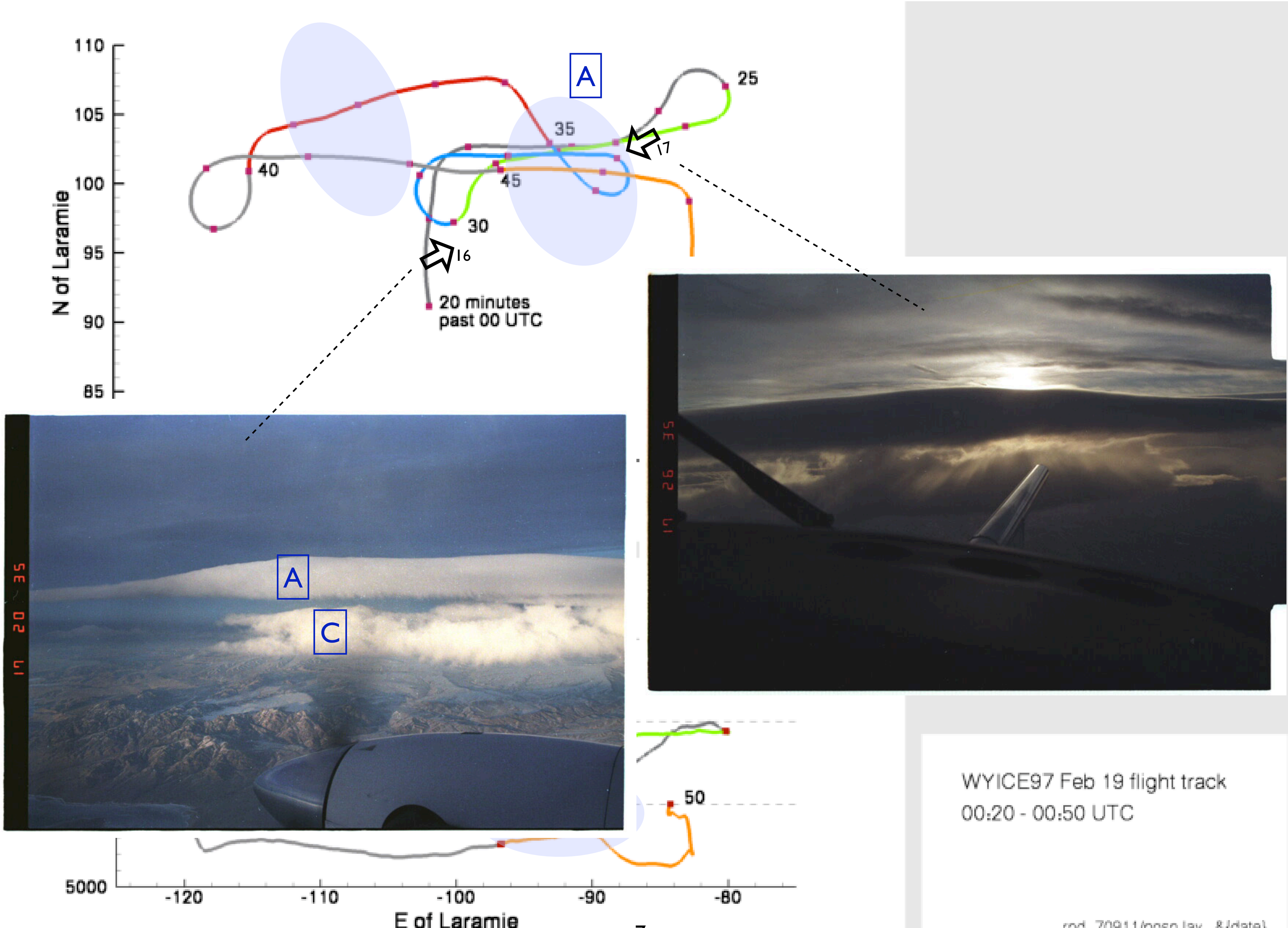



University of Wyoming King Air aircraft




WYICE97 Feb 19 flight track
00:20 - 00:50 UTC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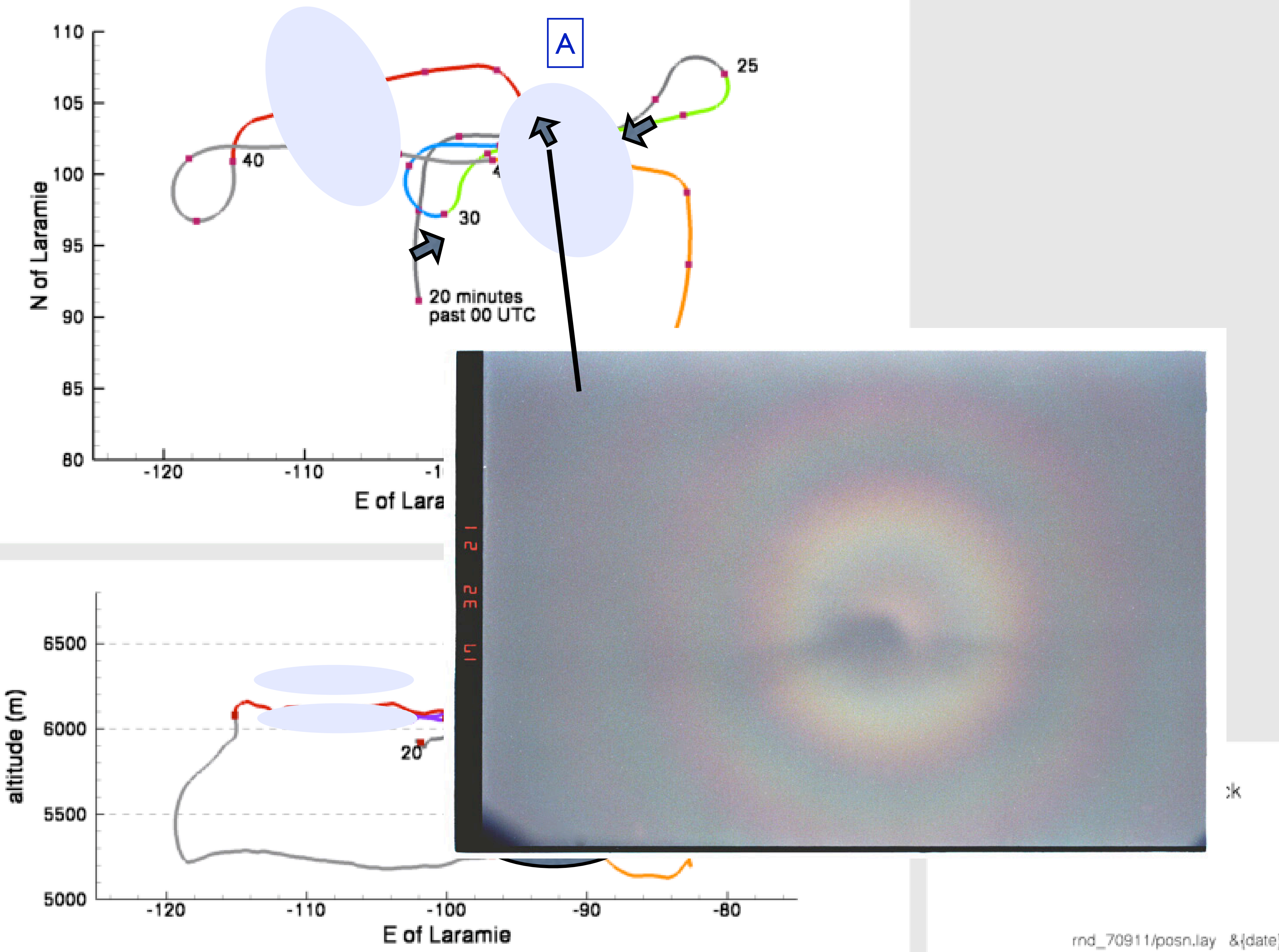
WYICE97 Feb 19 flight track
00:20 - 00:50 UTC
rnd_70911/posn.lay &{date}



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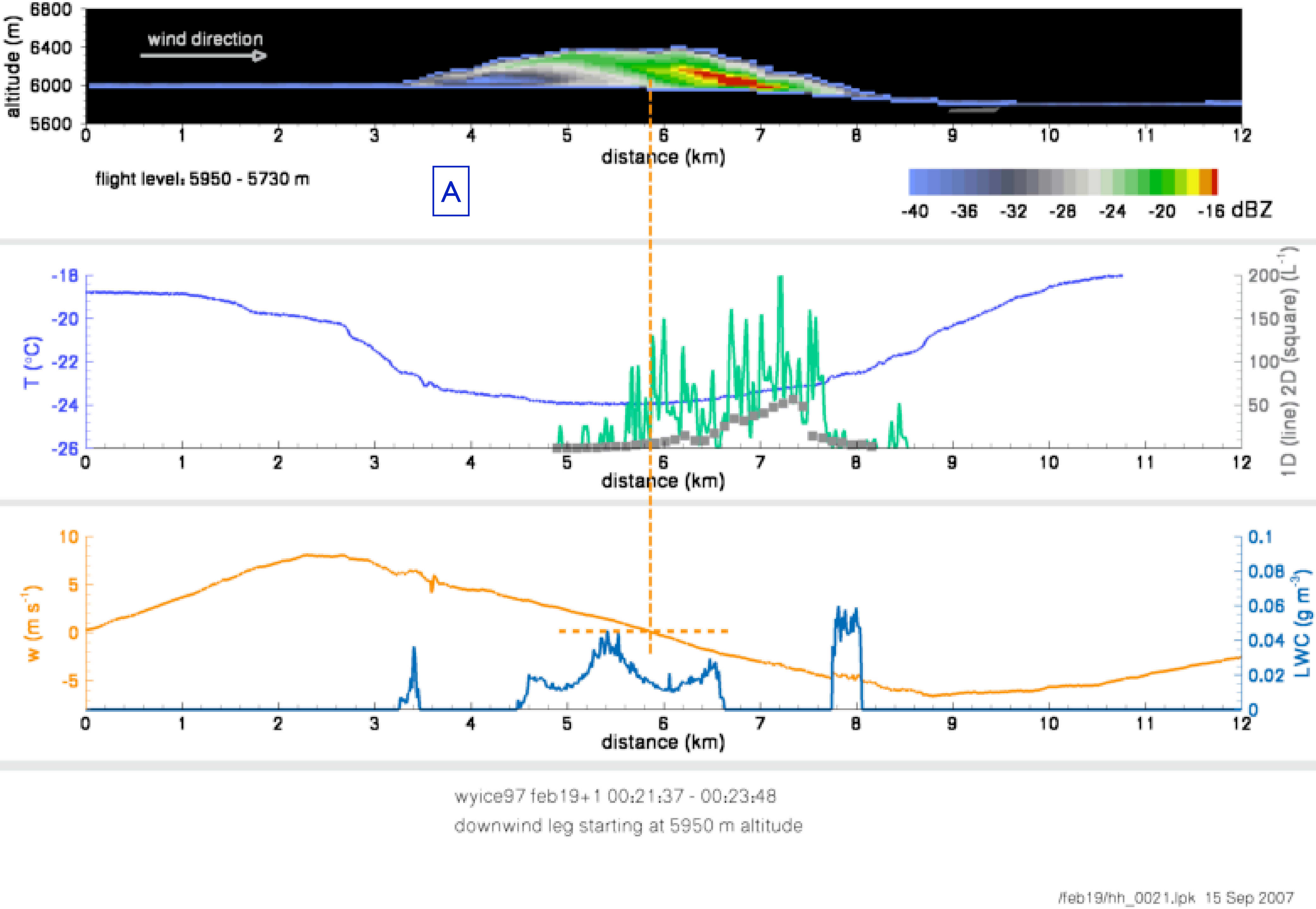
altitude (m)
wind direction
distance (km)
flight level: 5950 - 5730 m
A
-40 -36 -32 -28 -24 -20 -16 dBZ
T (°C)
1D (line) 2D (square) (L⁻¹)
w (m s⁻¹)
LWC (g m⁻³)
wyice97 feb19+1 00:21:37 - 00:23:48
downwind leg starting at 5950 m altitude
/feb19/hh_0021.lpk 15 Sep 2007

| Cloud | Time | Echo top | Penetration altitude | Est. min. temperature (°C) | LWC (g m$^{-3}$) | 2D ice conc. (L$^{-1}$) |
|---|---|---|---|---|---|---|
| A | 00:21 | 6400 m | 5800 m | −26 | ~ 0.05 | 50 |
| A | 00:27 | (horizontal beam) | 5930 m | −26 | ~ 0.05 | 35 |
| A | 00:32 | 6200 m | 6060 m | −25 | 0.10 | 5 |
| A | 00:34 | 6200 m | 6060 m | −25 | 0.12 | 2 |
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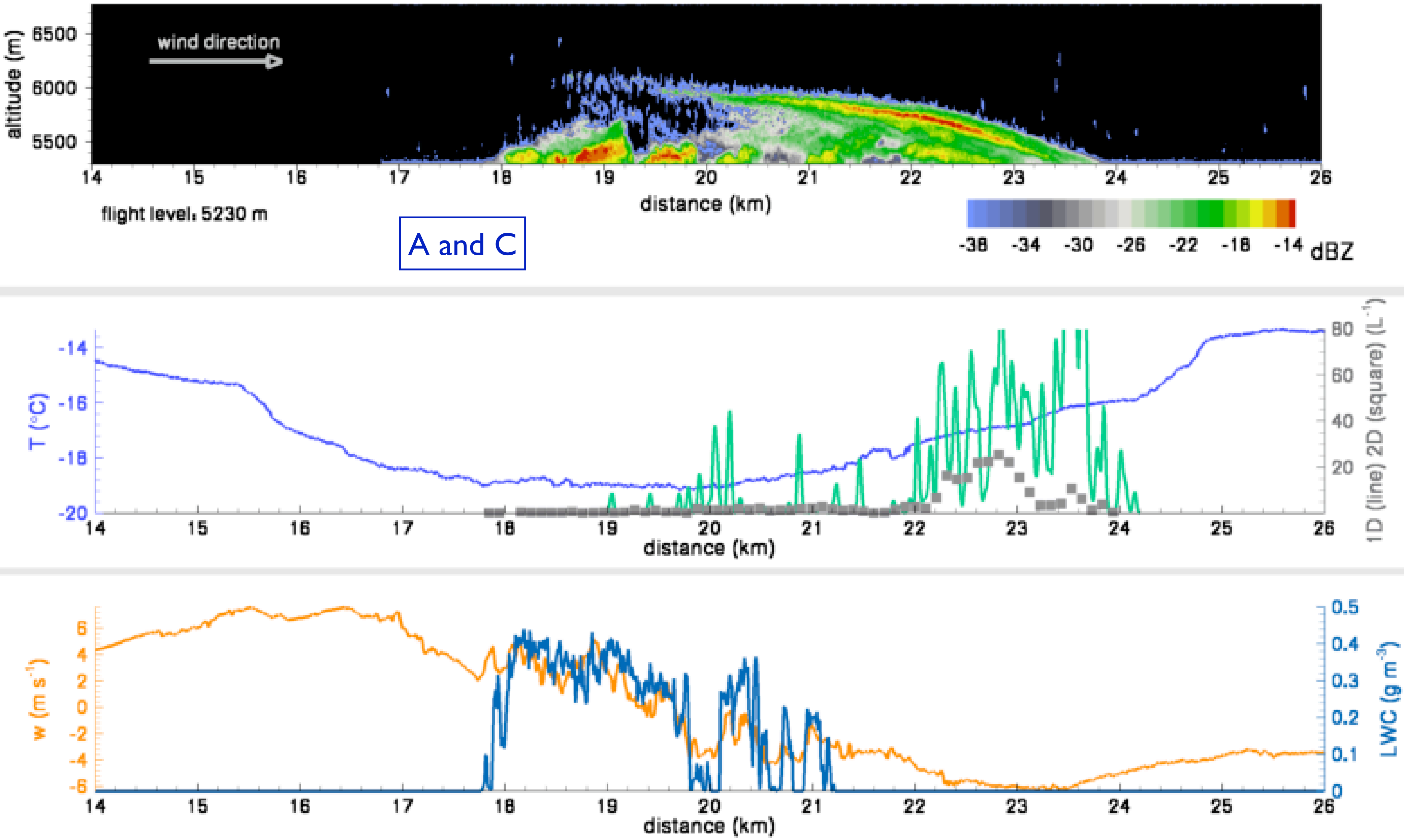
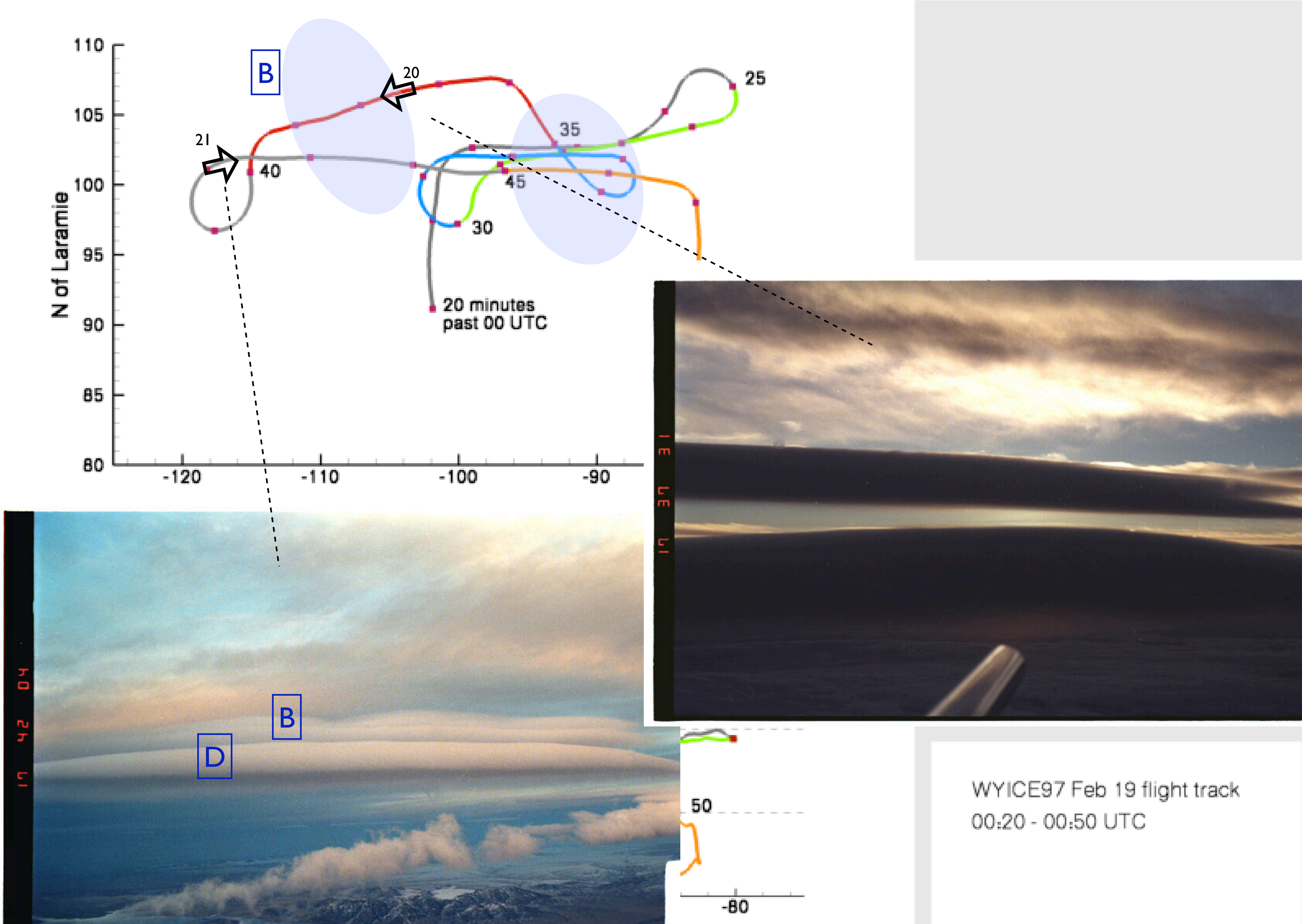
Change in composition accompany the lowering of the height of cloud top.

- shorter growth time, hence poorer detection
- real change in aerosol (ice nucleus) content




wyice97 feb19+1, 00:44:54 - 00:46:52

eastbound leg at 5230 m altitude



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20 minutes
past 00 UTC
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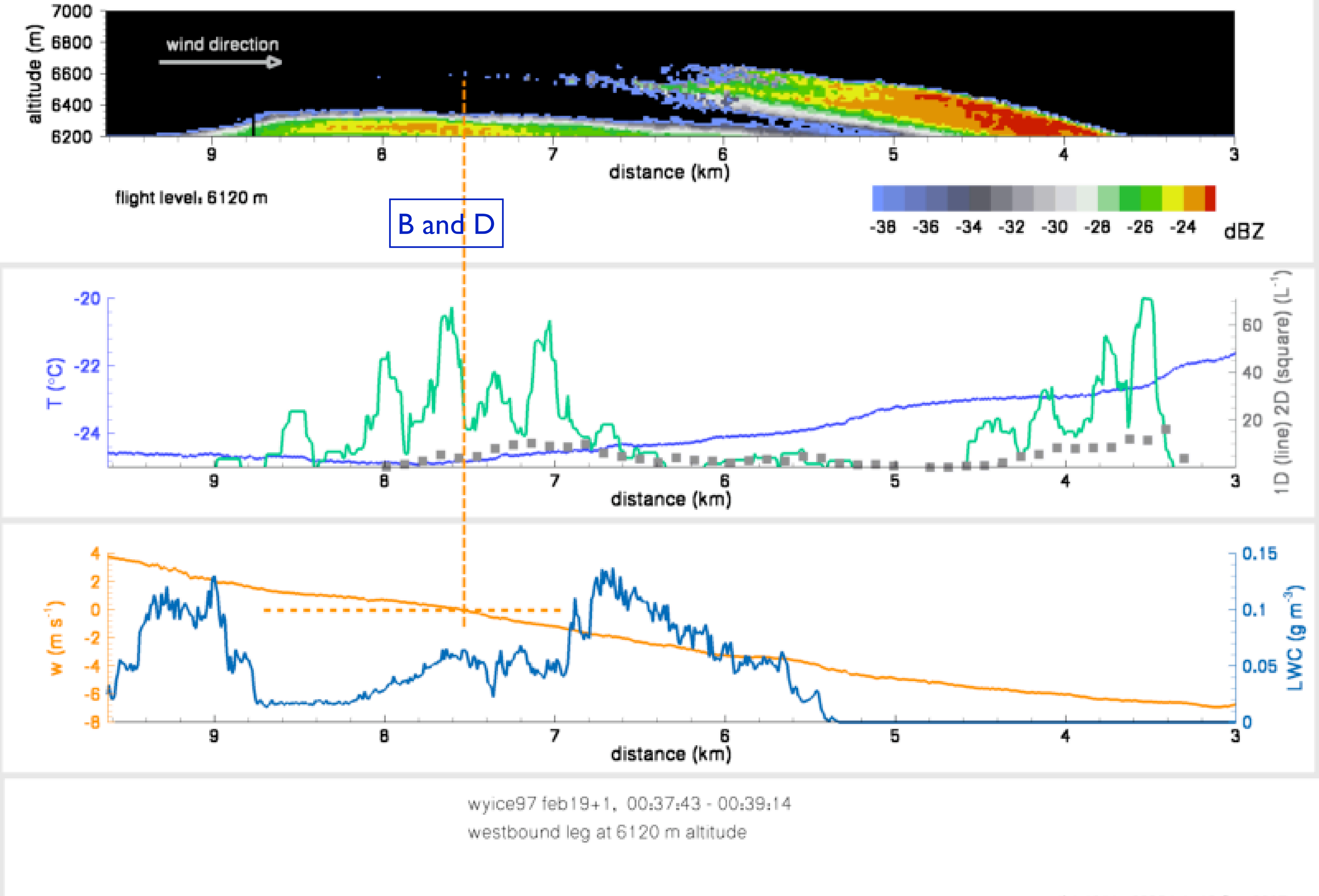
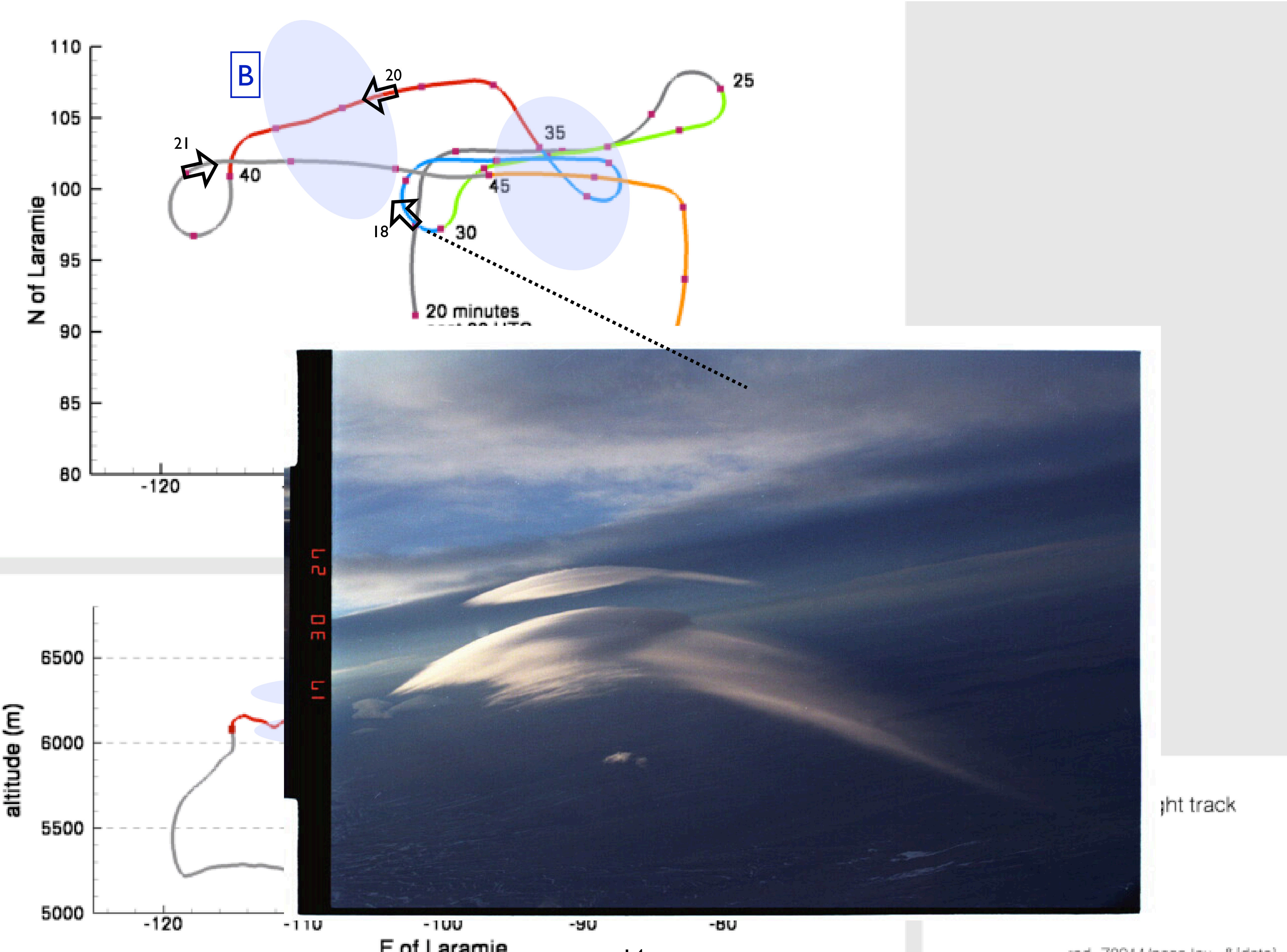
-80
WYICE97 Feb 19 flight track
00:20 - 00:50 UTC


altitude (m)
7000
6800
6600
6400
6200
wind direction
9
8
7
6
5
4
3
distance (km)
flight level: 6120 m
B and D
-38 -36 -34 -32 -30 -28 -26 -24
dBZ
T (°C)
-20
-22
-24
1D (line) 2D (square) (L⁻¹)
60
40
20
w (m s⁻¹)
4
2
0
-2
-4
-6
-8
LWC (g m⁻³)
0.15
0.1
0.05
0
wyice97 feb19+1, 00:37:43 - 00:39:14
westbound leg at 6120 m altitude
/feb19/hh_0036.lpk 16 Sep 2007



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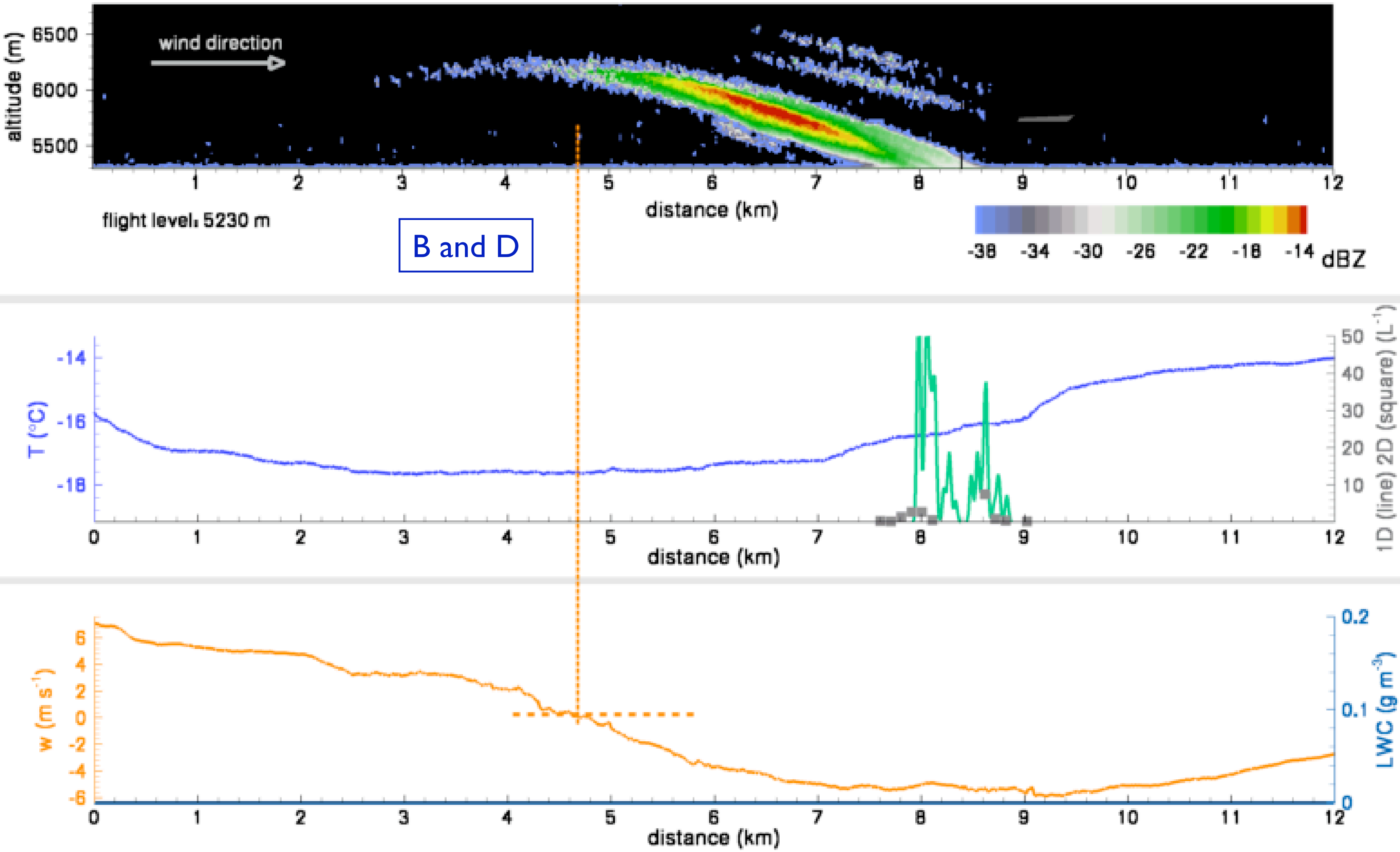


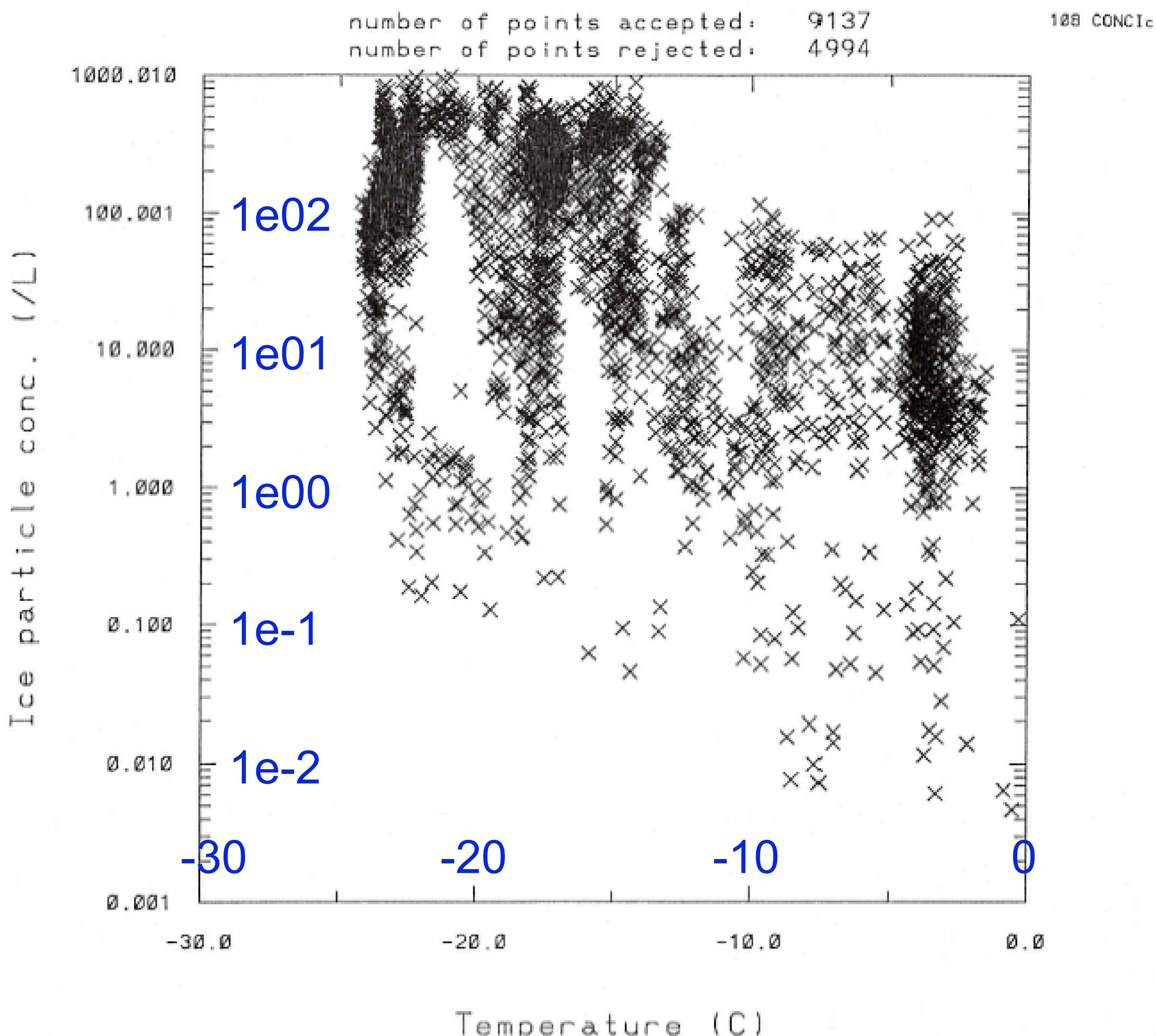

wyice97 feb19+1, 00:42:35 - 00:44:25
eastbound leg at 5230 m altitude

| Cloud | Time | Echo top | Penetration altitude | Est. min. temperature (°C) | LWC (g m$^{-3}$) | 2D ice conc. (L$^{-1}$) |
|---|---|---|---|---|---|---|
| A | 00:21 | 6400 m | 5800 m | −26 | ~ 0.05 | 50 |
| A | 00:27 | (horizontal beam) | 5930 m | −26 | ~ 0.05 | 35 |
| A | 00:32 | 6200 m | 6060 m | −25 | 0.10 | 5 |
| A | 00:34 | 6200 m | 6060 m | −25 | 0.12 | 2 |
| B | 00:37 | 6900 m | 6120 m | −28 | 0 | 15 |
| D | 00:39 | 6400 m | 6120 m | −26 | 0.12 | 10 |
| D | 00:42 | 6400 m | 5200 | −16 | | (6) in evap. trail |
| C | 00:44 | 5700 m (conv.) | 5230 | −21 | 0.4 | 2 |

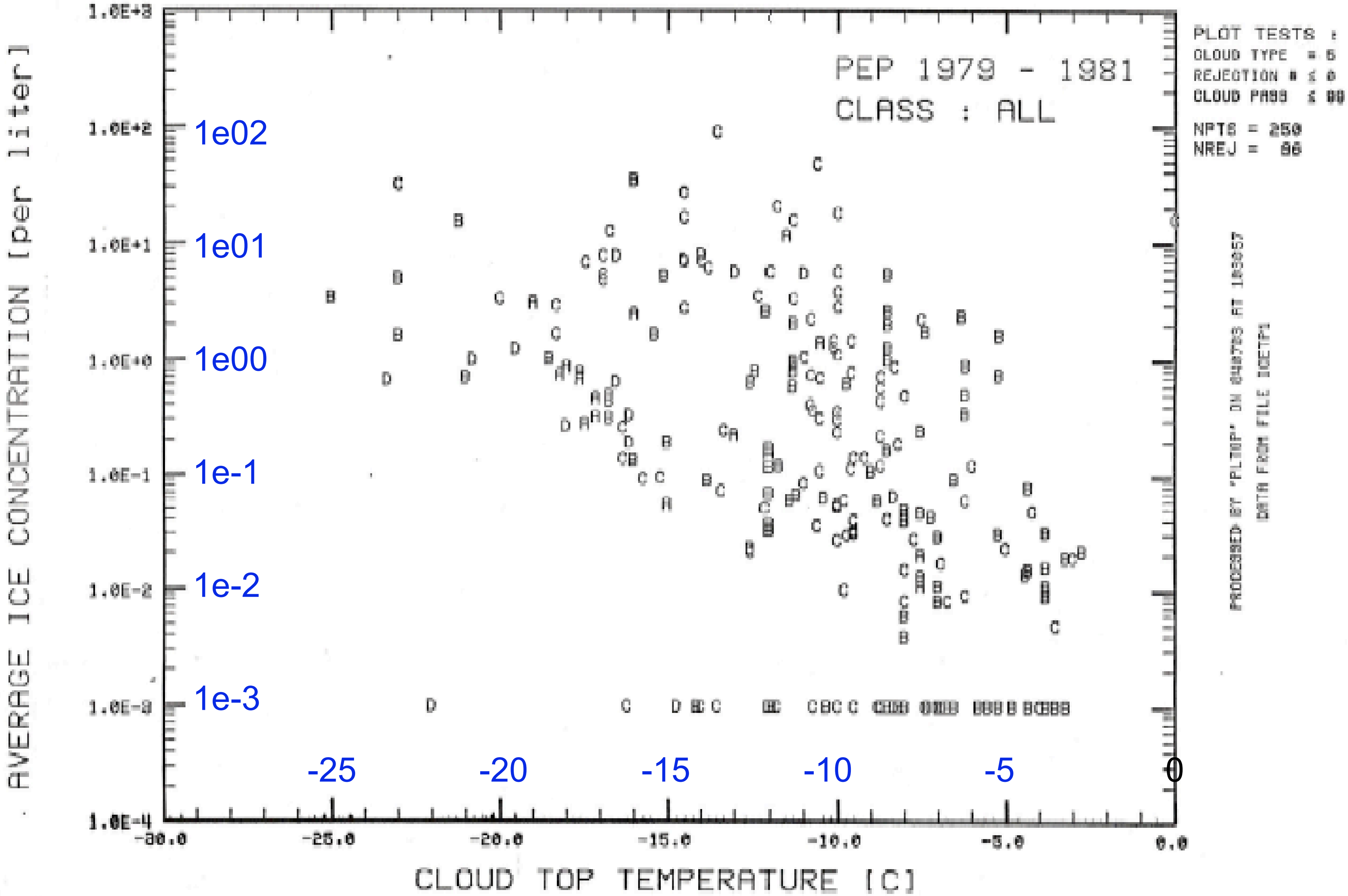
Rough indication of temperature trend, as expected.

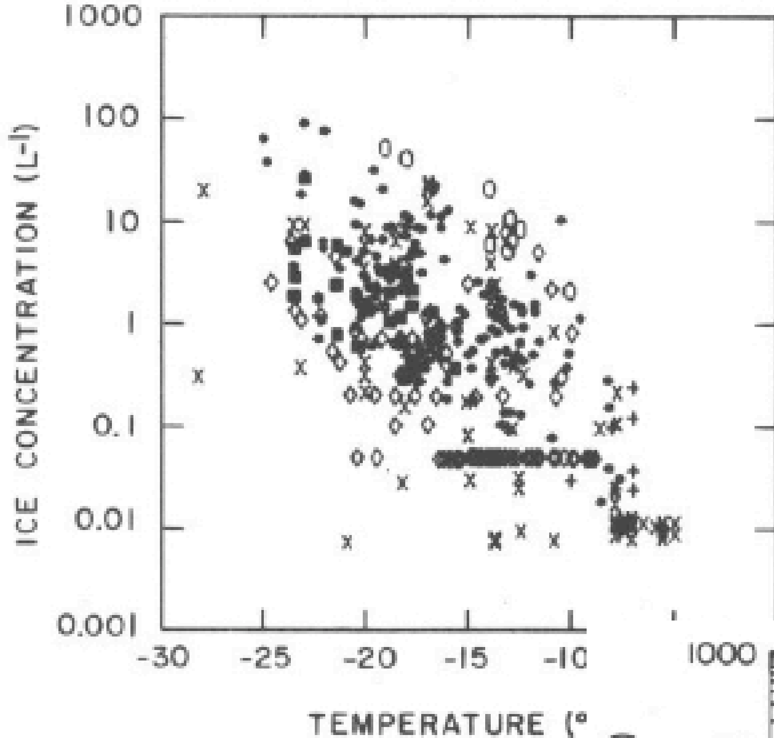
Given the complexities of clouds and the limitation of measurement techniques, cloud structure need to be considered, and data scrutiny is essential.

# One Cb over the Asir Mountains, Saudi Arabia



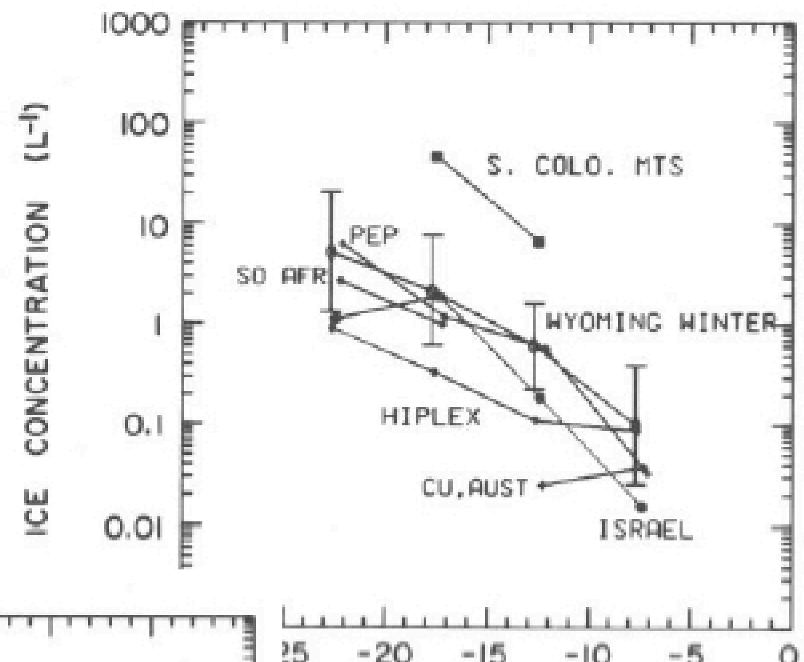
# Summary of ice concentrations by cloud types - Duero Basin, Spain

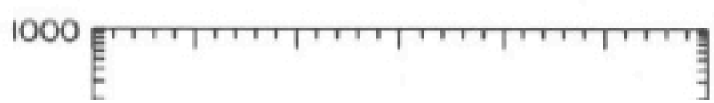





## Cooper,1986

**for cases where ice concentration can be attributed to nucleation**



Size distribution of germs : $N(n) = N_o \, e^{-\Delta G(n)/kT}$

Nucleation rate : $J = A \; e^{-\Delta G^* /kT}$ $[L^{-3} T^{-1}]$

Deposition : $J = A \; exp\left[ - B \dfrac{\sigma^3}{T^3} \dfrac{1}{(\ln S)^2} \right]$

Freezing : $J = A_f \, \sigma_{i/w}^{1/2} \; exp\left[ - B_f \dfrac{\sigma_{i/w}^3}{kT} \dfrac{1}{\{\ln[T_0/T]\}^2} \right]$

Jeffery and Austin (1997)

# How to determine ***J*** experimentally ??

Approach A: Bring to *S* or *T* a large number of *identical* volumes with the same *probability* of containing an *identical* nucleus.

Approach B: Repeated exposure of the same sample to the same *S* or *T*, assuming that *the* nucleus remains unaltered.

Both approaches have to accept that *S* or *T* has to be reached at some finite rate from the stable state of the parent substance, i.e. $S$=0 or $T$=0

Koop 2004 (Z. Phys. Chem):

# Differential scanning calorimetry of emulsion of water in oil

A

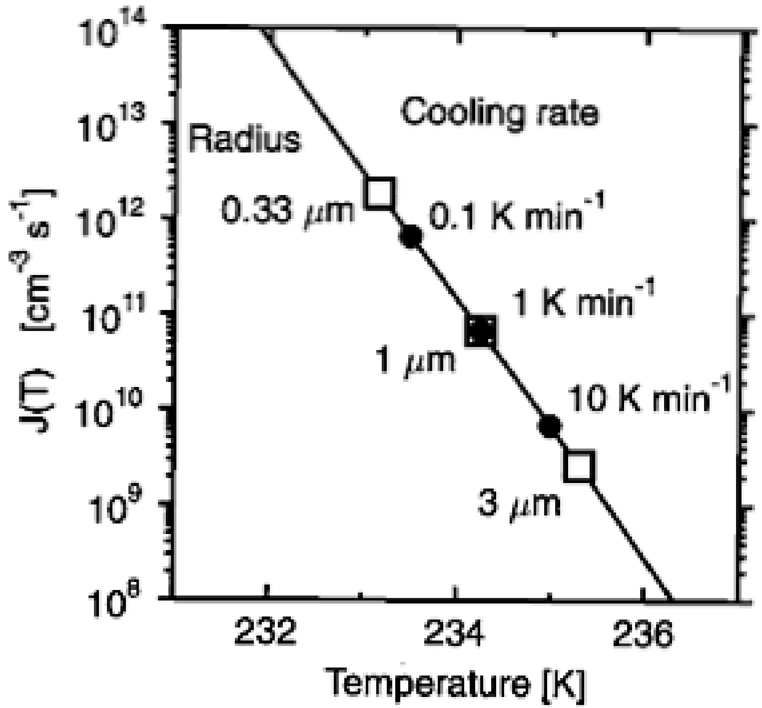



**Fig. 14.** The homogeneous volume nucleation rate coefficient of ice in water, $J(T)$, as a function of temperature (black line [95]). The data points indicate the median freezing temperatures of water droplets for various conditions; squares: for droplets of different size at a cooling rate of 1 K min$^{-1}$, circles: for different cooling rates and a droplet with a radius of 1 μm.

Benz et al. 2005 (J. Photochem. Photobiol.)

# Cloud chamber observation of rate of ice formation

A

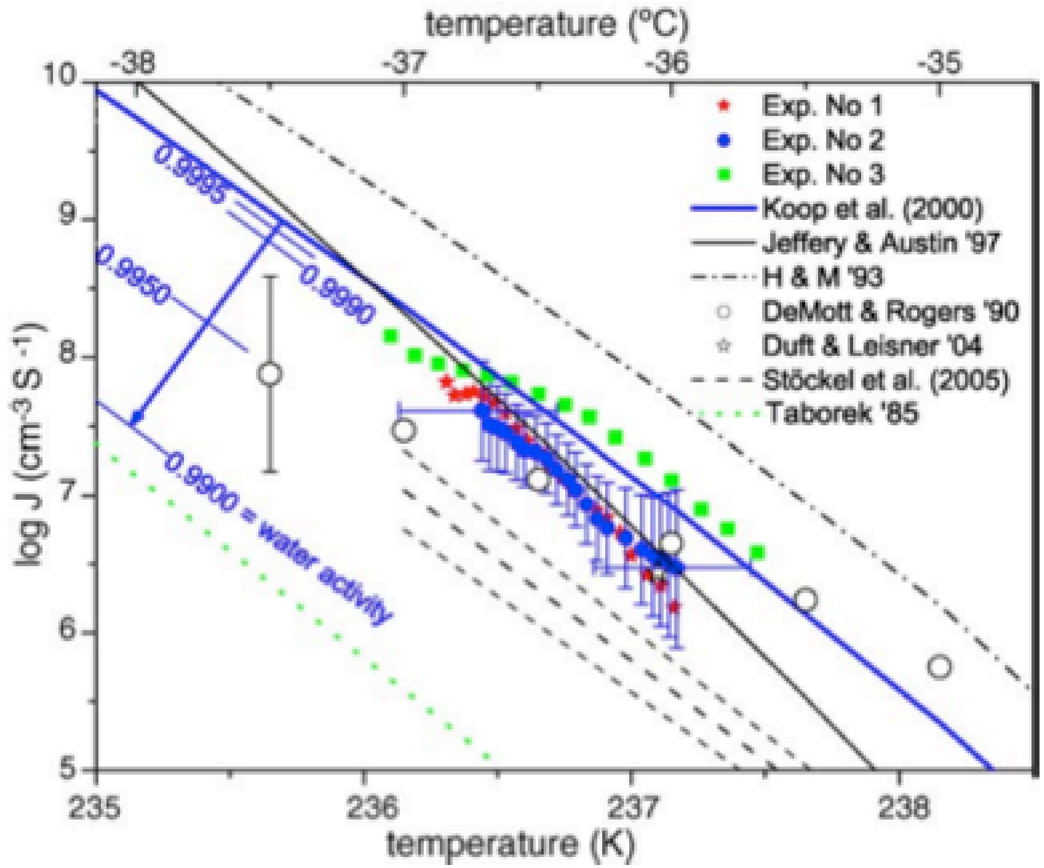



Fig. 8. Filled symbols: nucleation rates $J(T)$, this work, including corrections for all *known* systematic uncertainties, error bars shown for one experiment only. Thick solid line: parameterisation of the nucleation rate by Pruppacher [10] and adopted by Koop et al. [35] in their parameterisation of $J(T,a)$, as explained in text; thin solid line: parameterisation proposed by Jeffery and Austin [13]; dash-dotted line: parameterisation based on measurements in clouds by Heymsfield and Miloshevich (H & M) [26]; large open circles: cloud chamber study by DeMott and Rogers [19]; dashed line with error range (thin dashed lines): levitated droplet measurements by Stöckel et al. [36]; open star: levitated droplet measurement by Duft and Leisner [18]. Short dashed line in lower left corner: emulsified droplet measurements of Taborek [37].

Source: Seeley and Seidler, 2001 (Phys. Rev. Lett.)

# Repeated freezing of a single drop with long chain alcohol monolayer during cycles of steady cooling.

rate = number freezing within interval / number not frozen at that temperature

B

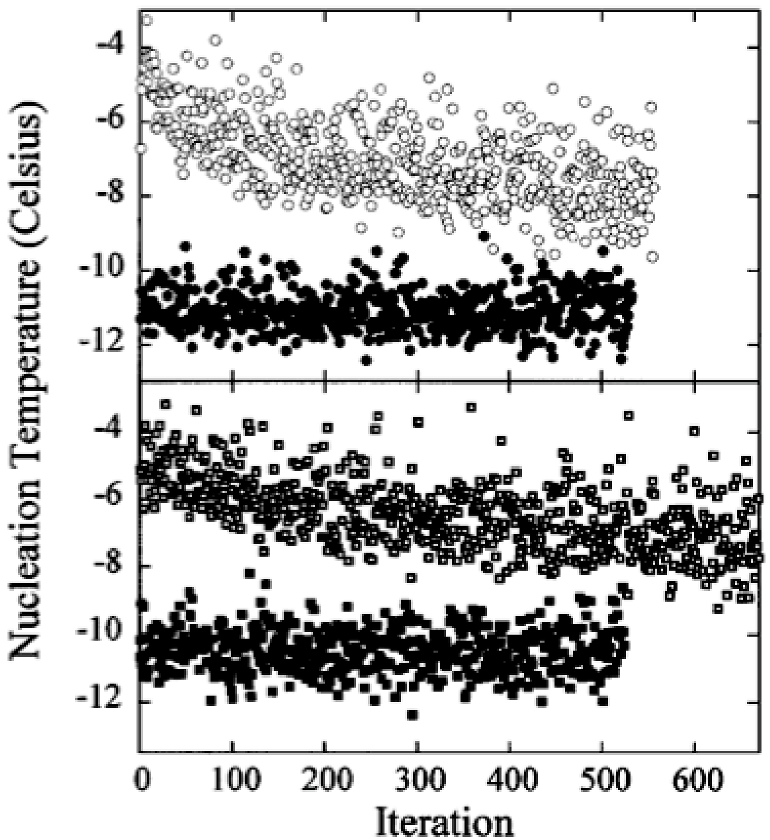



FIG. 1. The nucleation temperature as a function of iteration number for a 10 $\mu$L water sample containing $2.5 \times 10^{-10}$ mol of (○) pentacosanol ($C_{25}H_{52}O$), (●) hexacosanol ($C_{26}H_{54}O$), (□) heptacosanol ($C_{27}H_{56}O$), and (■) octacosanol ($C_{28}H_{58}O$).

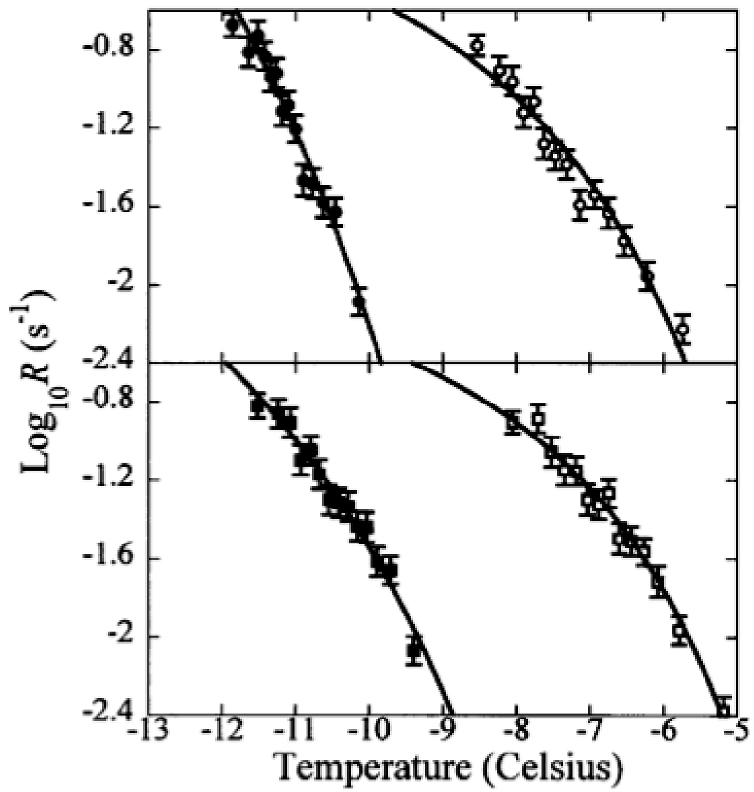



FIG. 2. The freezing rate as a function of temperature for a 10 $\mu$L water sample containing $2.5 \times 10^{-10}$ mol of (○) pentacosanol ($C_{25}H_{52}O$), (●) hexacosanol ($C_{26}H_{54}O$), (□) heptacosanol ($C_{27}H_{56}O$), and (■) octacosanol ($C_{28}H_{58}O$). As described in the text the solid lines represent the best-fit curves of Eq. (5) to the experimental data.

Source: Zobrist, Koop, Luo, Marcolli, Peter 2007 (J. Phys. Chem.)

B

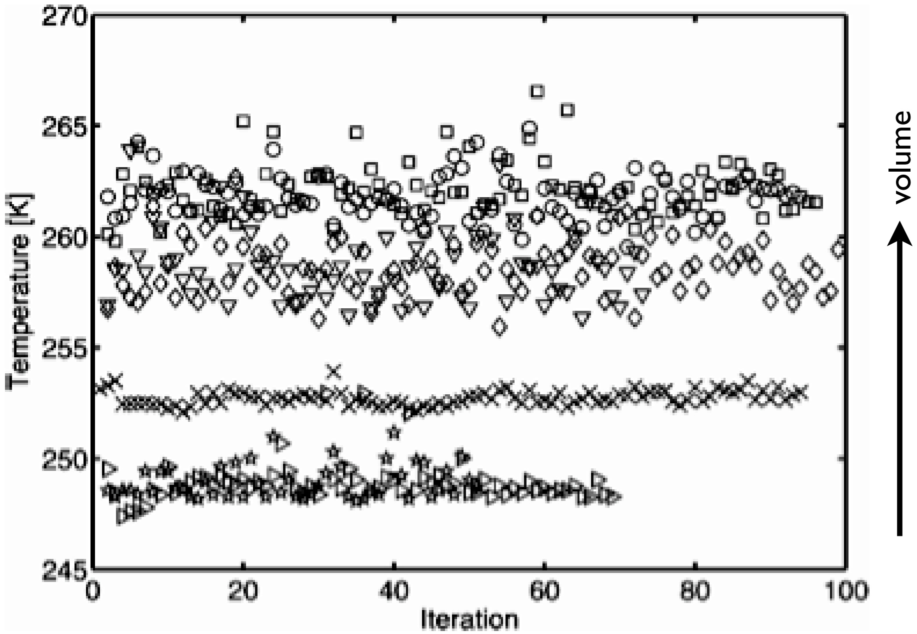



**Figure 1.** Measured freezing points for seven droplets exposed to cooling/heating cycles with 10 K min$^{-1}$ as a function of iteration number. Six droplets are coated with 1-nonadecanol, one remained uncoated. Coated droplets: (circles and squares) $r$ = 1100 $\mu$m; (diamonds and downward-pointed triangles) $r$ = 370 and 320 $\mu$m, respectively; and (stars and right-pointed triangles) $r$ = 31 and 48 $\mu$m, respectively. Uncoated droplet: (crosses) $r$ = 1100 $\mu$m.

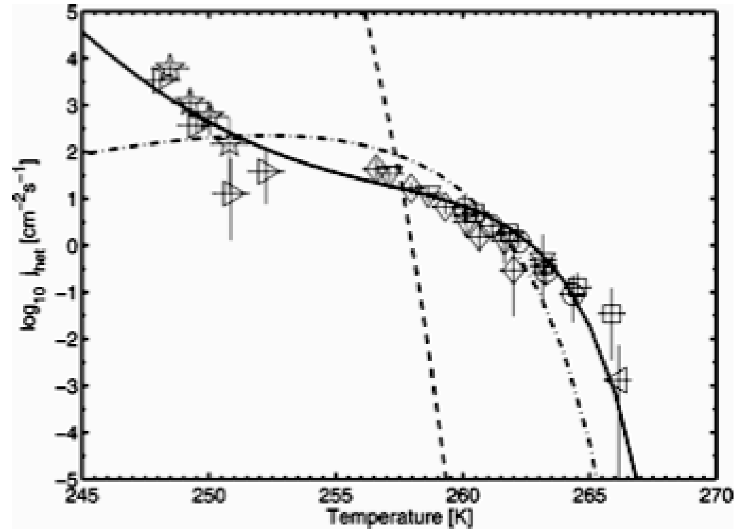



**Figure 3.** Measured heterogeneous ice nucleation rate coefficients for six single water droplets coated with nonadecanol as a function of temperature. The symbols are the same as in Figure 1. The horizontal and vertical thin lines are the errors in temperature and the uncertainties due to the Poisson statistics on the 95% level, respectively. Additionally, an isothermal measurement of $j_{het}$ (left-pointed triangle) at 266.15 K is shown.[25] (Dashed line) Best fit of the CNT with a constant $\alpha$ of 52.4°. (Solid line) Best fit of the CNT with $\alpha$ as a linear function of temperature (see Figure 4). (Dashed dotted line) Best fit with the approach of Seeley and Seidler.[8]

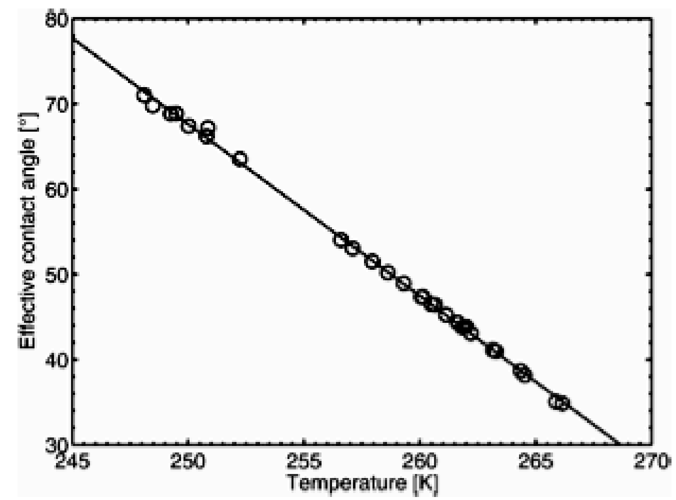



**Figure 4.** (Circles) Calculated $\alpha$ values for water droplets coated with nonadecanol as a function of temperature (see Table 1). (Solid line) Linear fit of the circles: $\alpha(T) = 571.50-2.015T$, where $T$ is given in Kelvin. $\alpha$ is given in degree and the function is valid for 248 K $\leq T \leq$ 268 K.

3.5
1 2 3 4
1.5 2.5 3.5
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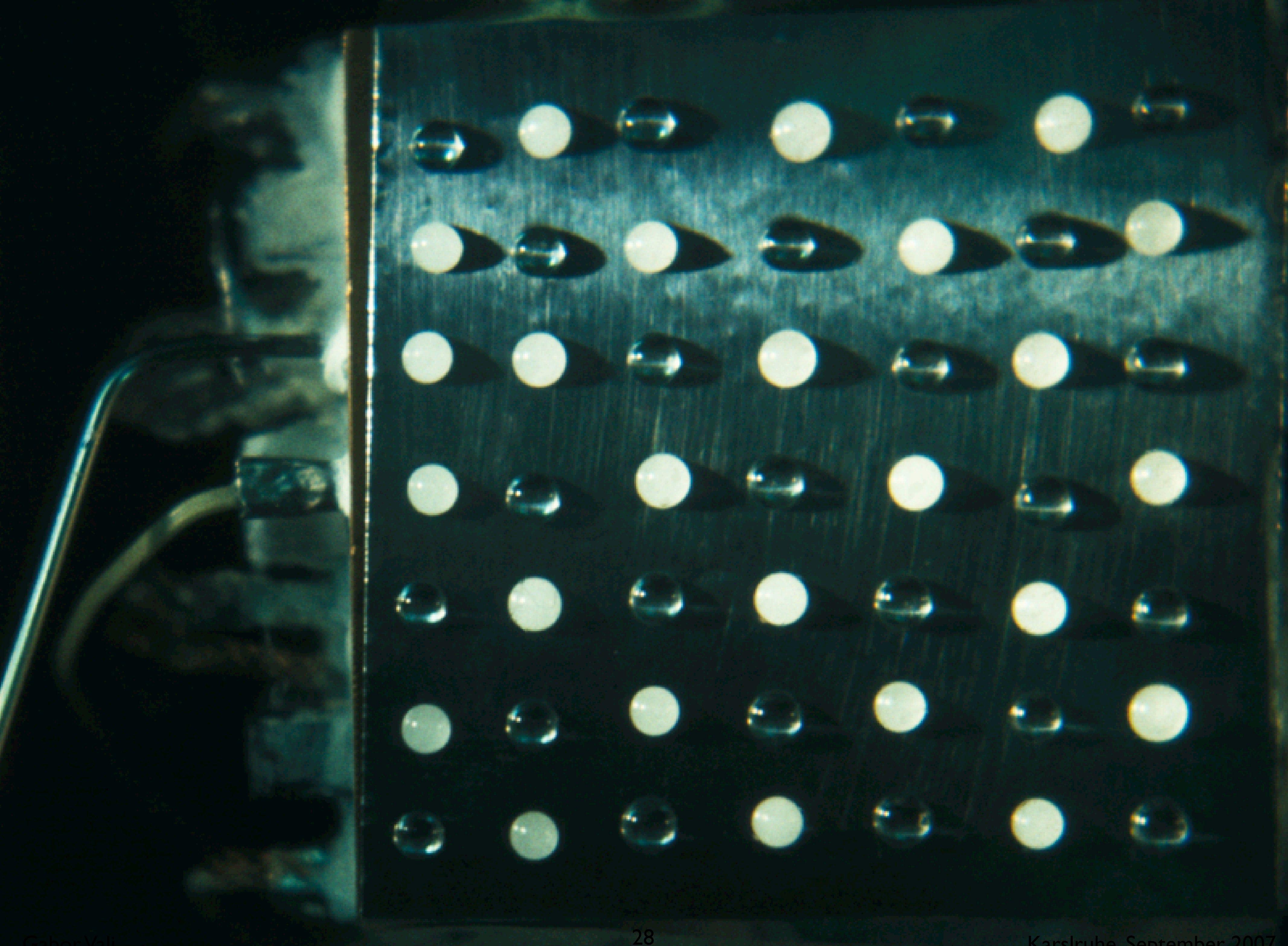
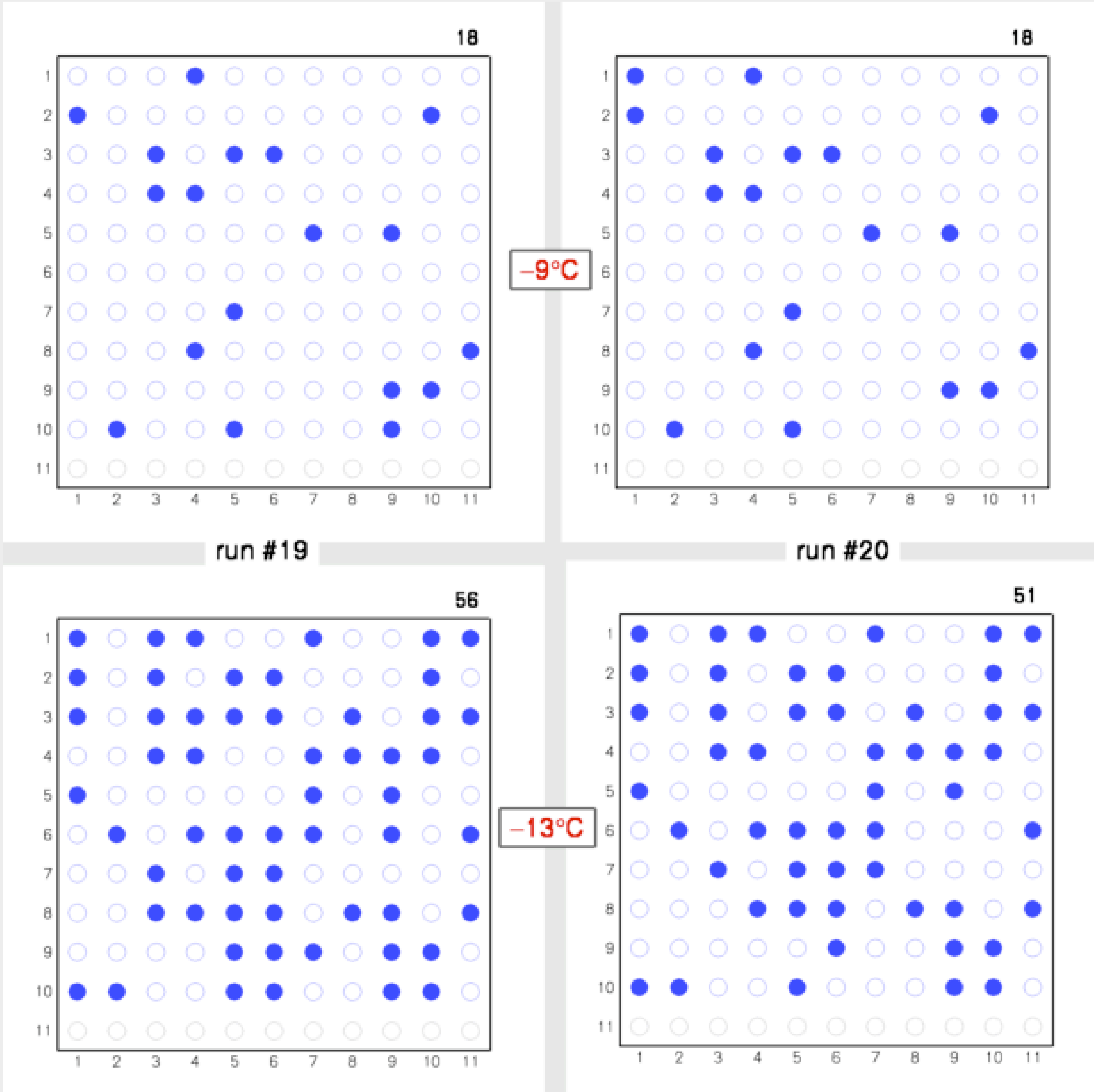
3 4 5

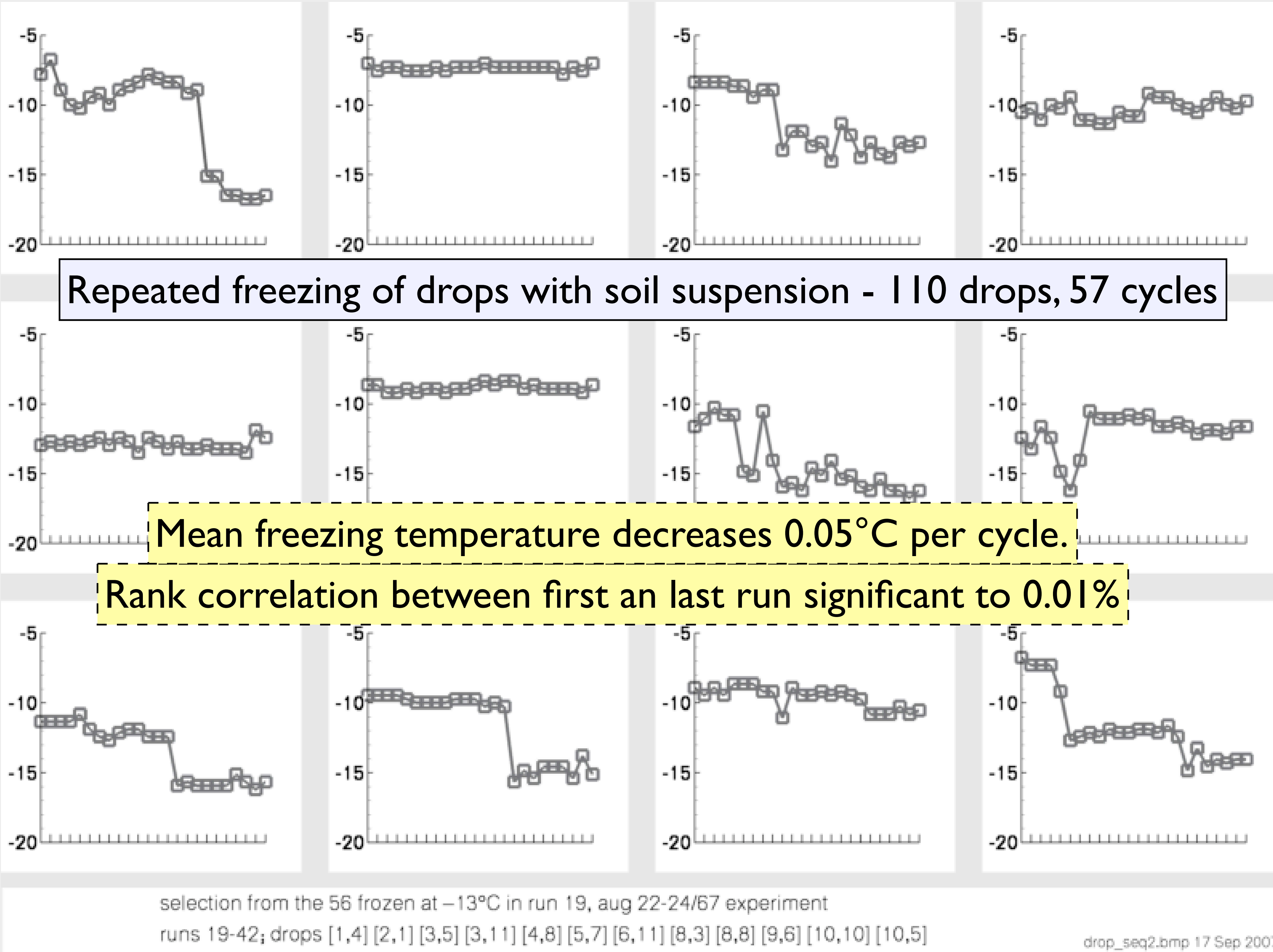


B




frozen drops (filled circles) at −9 and −13°C in two consequtive runs
distilled water control drops in bottom row (gray circles)
aug22-24/67 experiment with soil suspension

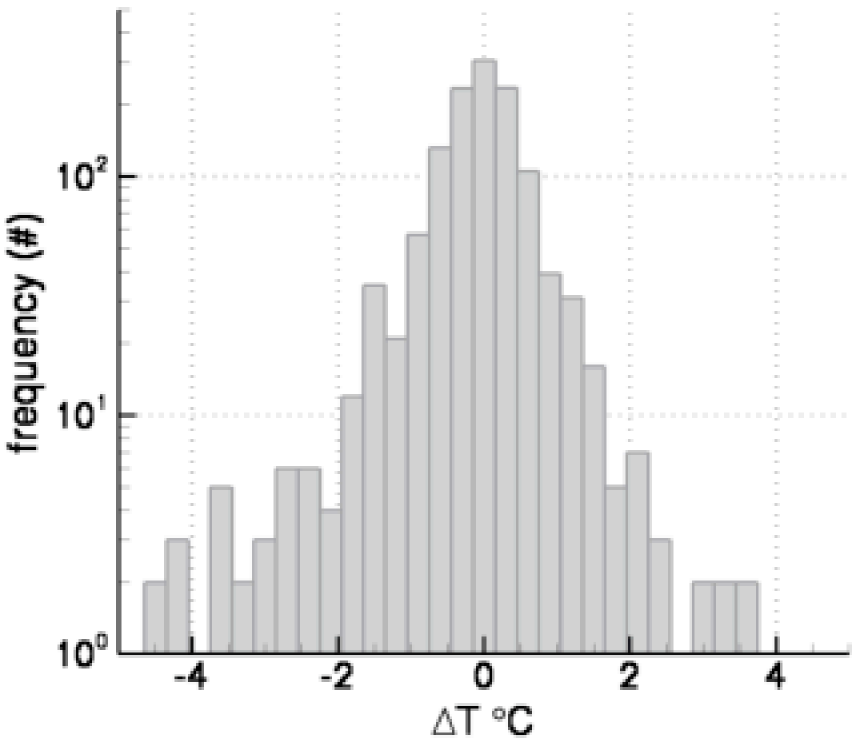
## Repeated freezing of drops with soil suspension - 110 drops, 57 cycles

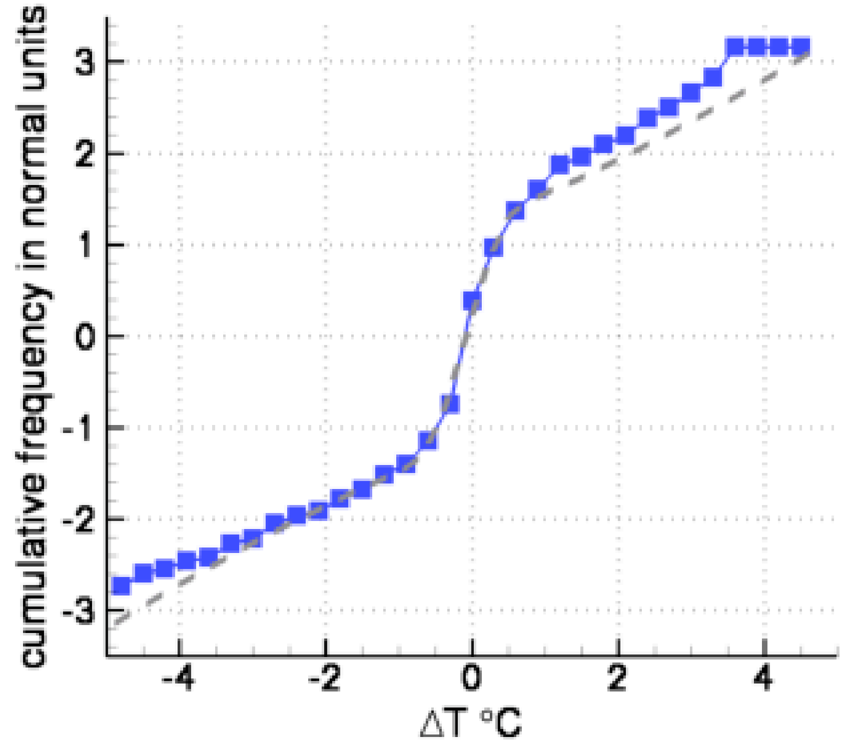



selection from the 56 frozen at –13°C in run 19, aug 22-24/67 experiment
runs 19-42; drops [1,4] [2,1] [3,5] [3,11] [4,8] [5,7] [6,11] [8,3] [8,8] [9,6] [10,10] [10,5]

**Mean freezing temperature decreases 0.05°C per cycle.**

**Rank correlation between first an last run significant to 0.01%**




change in freezing temperature from one run to the next

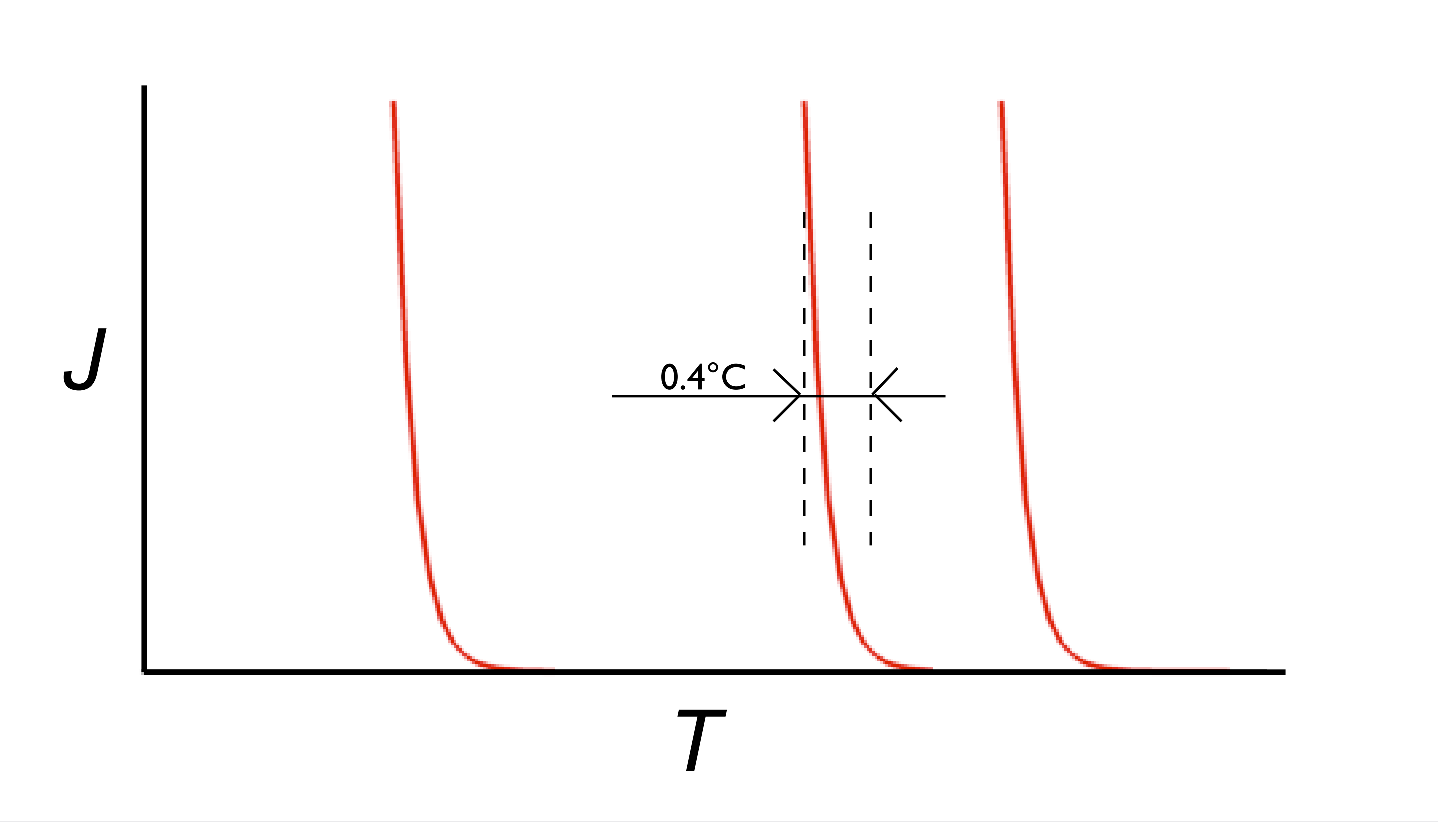
statistics of run-to-run changes for drops with fr-temps >-13°C in run 19
runs 19 - 42 from aug 22-24, 1967 experiment with soil suspension
total 1284 events (56 drops in 24 runs; 4 missing), 4 with $\Delta T<-4.8$, 2 with $\Delta T>4.8$
fit with $\sigma_1 = 0.28$, $\sigma_2 = 1.8$, $w_1 = 0.78$ and offset of -0.09°C

Random variation with σ = 0.28°C accounts for 78 % of observations.
The remainder is roughly described by normal pdf with = σ 1.8°C

for normal distribution:

$$\sigma(x_i - x_j) \approx 1.4 \times \sigma(x_i - \langle x \rangle)$$

The contribution of stochastic fluctuations in embryo growth to the determination of freezing temperatures is ± 0.2°C, on top of a temperature determined by the singular properties of the nucleus. This can be seen in terms of a nucleation rate *J* rising sharply within that narrow temperature interval, with the characteristic temperature fixing the base temperature.



## Positives:

- alcohol monolayer, soil, silver iodide, *Ps. syr.* results are very similar
- by separating the effect of molecular fluctuations from alterations of the nuclei with time, the nucleation rate $J$ is found to be a steeper function of temperature then in previous work

## Unresolved:

- better definition of the form of the rate function
- reconcile with dependence on cooling rate
- temperature dependence of the rate function

## Consequences

- The rate function is not a unique property of the substance, but has to be formulated/adjusted specifically to every nucleus/site (singularity). As an approximation this may be an additive term to temperature.
- Fitting a rate function to observations from repeated freezing of single drops that assumes that the nucleus remains unaltered during the process can lead to erroneous results.