Influence of particle surface modification on the immersion freezing behavior of supercooled droplets

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Content

- Motivation
- FROST - LACIS measurement setup
- Results
- Conclusion and Outlook

- Ice containing clouds permanently cover 40% of the earth surface.

  → large impact on precipitation, cloud electrification and radiation balance.

- Different ice forming processes exist: homogeneous and heterogeneous ice nucleation.

- Our understanding of physical and chemical processes underlying heterogeneous ice formation is limited (Kärcher and Lohmann, 2003).

  → more scientific work is necessary.

- Measurements with LACIS:
  - Immersion freezing measurements
  - Investigation of well-defined particles
  - Only one particle per droplet

- Scientific Questions: FROST I and II
  - Mineral dust particles act effectively as Ice Nuclei (IN) → Do coatings with acids change the surface of dust particles and therefore their IN ability?
  - How does IN ability change if particles are thermally treated?
  - Is heterogeneous ice nucleation a stochastic process (stochastic hypothesis) or does ice nucleation occur on specific sites at characteristic temperatures (singular hypothesis)?

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- FROST II: FReezing Of duST II

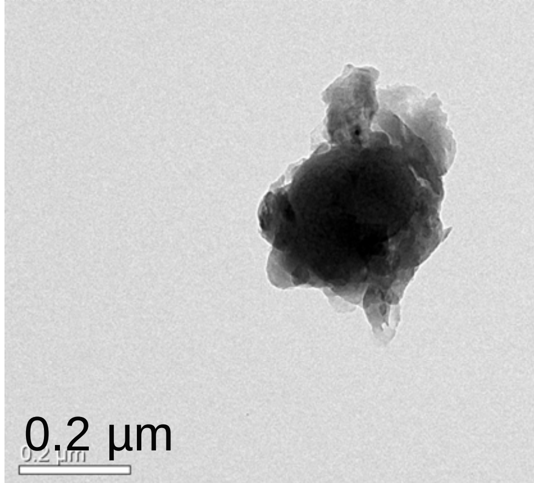
Immersion freezing	→	- CFDC (CSU) - LACIS (IfT)
Deposition nucleation	→	- CFDC (CSU) - PINC (ETH Zurich) - FINCH (Uni. of Frankfurt)
Hygroscopic growth	→	- H-TDMA (FZ Jülich)
Activation	→	- CCNc (IfT)
Chemical composition	→	- AMS (Uni. of Mainz) - ATOFMS (ETH Zurich)

- FROST II: FReezing Of duST II

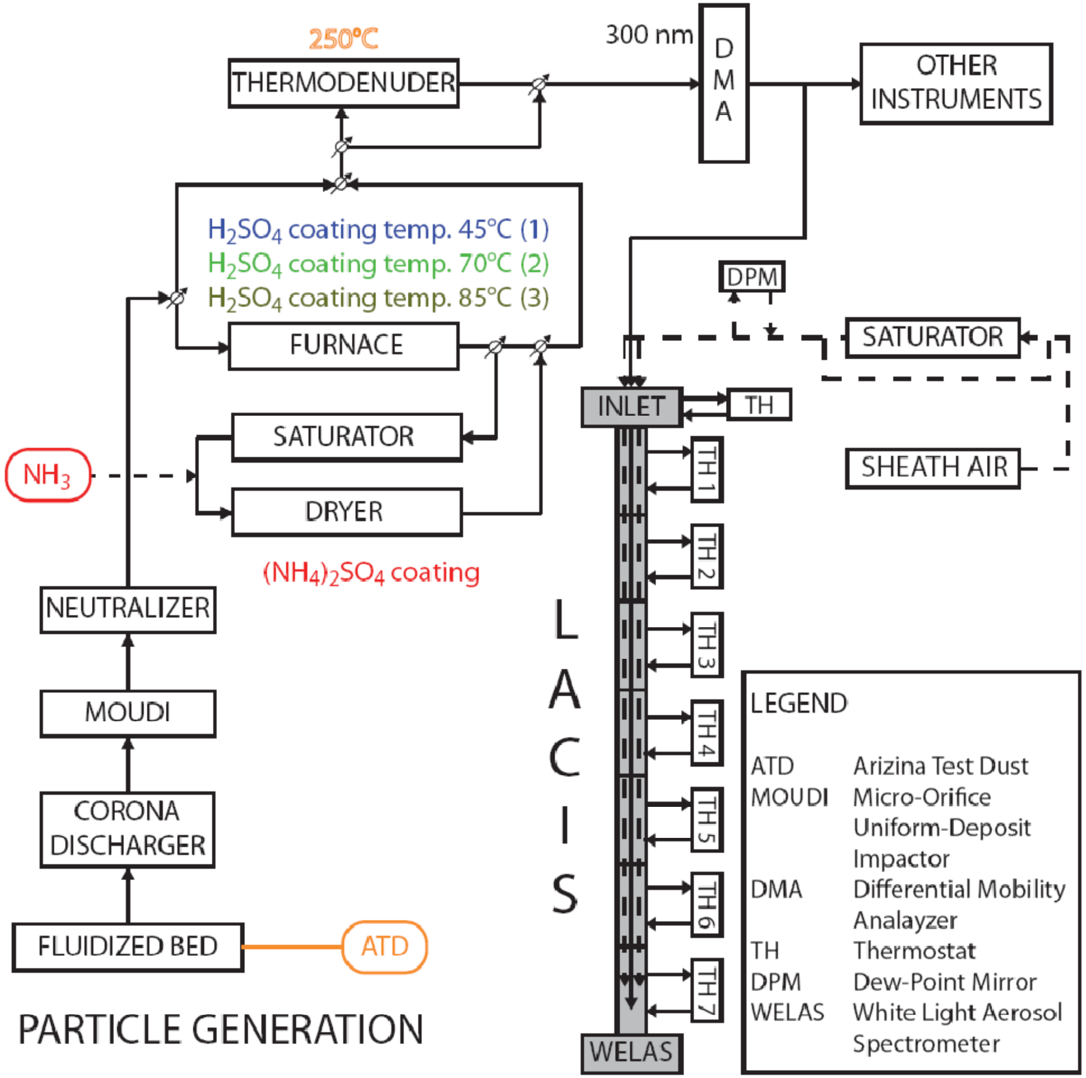
  – Arizona Test Dust (ATD) particles D_{mob} = 300nm

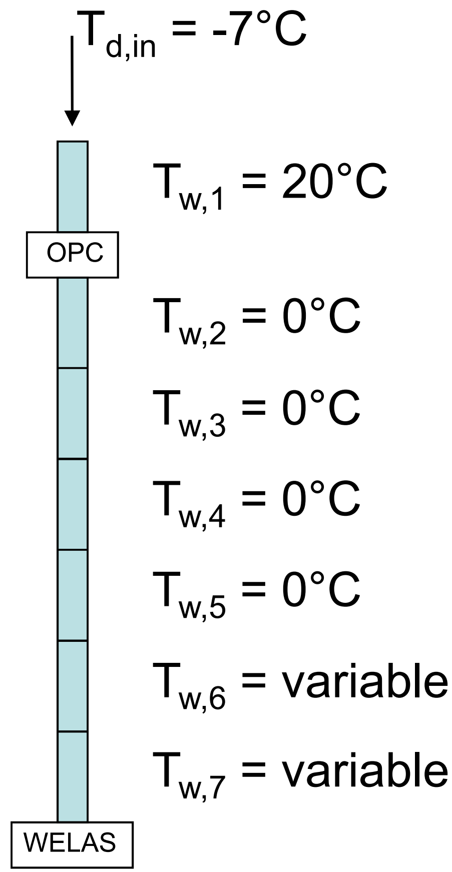
  – Various coatings: Uncoated, H_2SO_4 (3 coating conditions), $(NH_4)_2SO_4$

  – Thermal treatment using a thermodenuder at 250°C



ATD: SiO_2, Al_2O_3, ...


250°C
THERMODENUDER
300 nm
DMA
OTHER INSTRUMENTS
H_2SO_4 coating temp. 45°C (1)
H_2SO_4 coating temp. 70°C (2)
H_2SO_4 coating temp. 85°C (3)
FURNACE
SATURATOR
NH_3
DRYER
$(NH_4)_2SO_4$ coating
NEUTRALIZER
MOUDI
CORONA DISCHARGER
FLUIDIZED BED
ATD
PARTICLE GENERATION
DPM
SATURATOR
INLET
TH
SHEATH AIR
TH1
TH2
TH3
TH4
TH5
TH6
TH7
LACIS
WELAS
LEGEND
ATD Arizina Test Dust
MOUDI Micro-Orifice Uniform-Deposit Impactor
DMA Differential Mobility Analayzer
TH Thermostat
DPM Dew-Point Mirror
WELAS White Light Aerosol Spectrometer


$T_{d,in}$ = -7°C
$T_{w,1}$ = 20°C
OPC
$T_{w,2}$ = 0°C
$T_{w,3}$ = 0°C
$T_{w,4}$ = 0°C
$T_{w,5}$ = 0°C
$T_{w,6}$ = variable
$T_{w,7}$ = variable
WELAS

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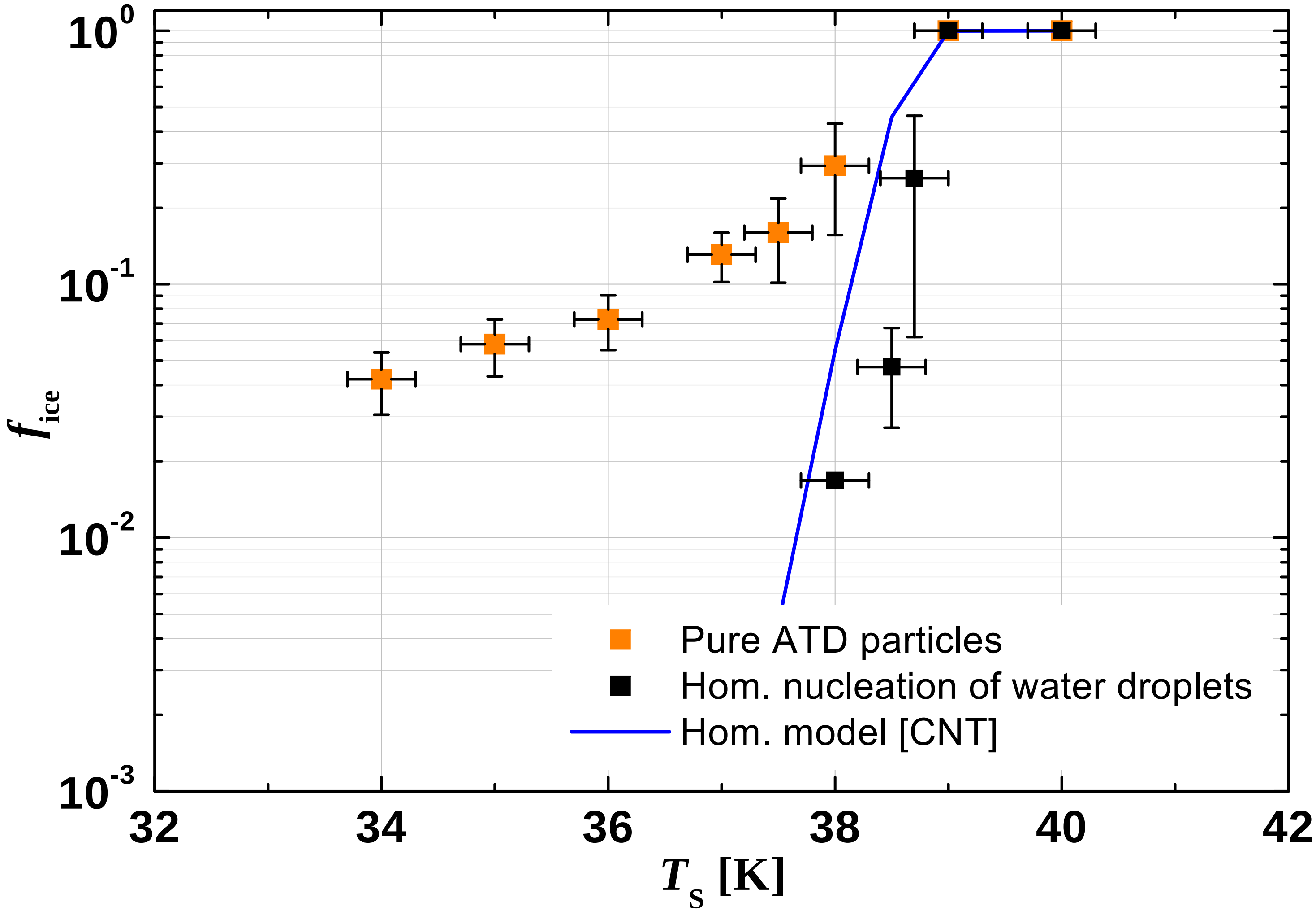
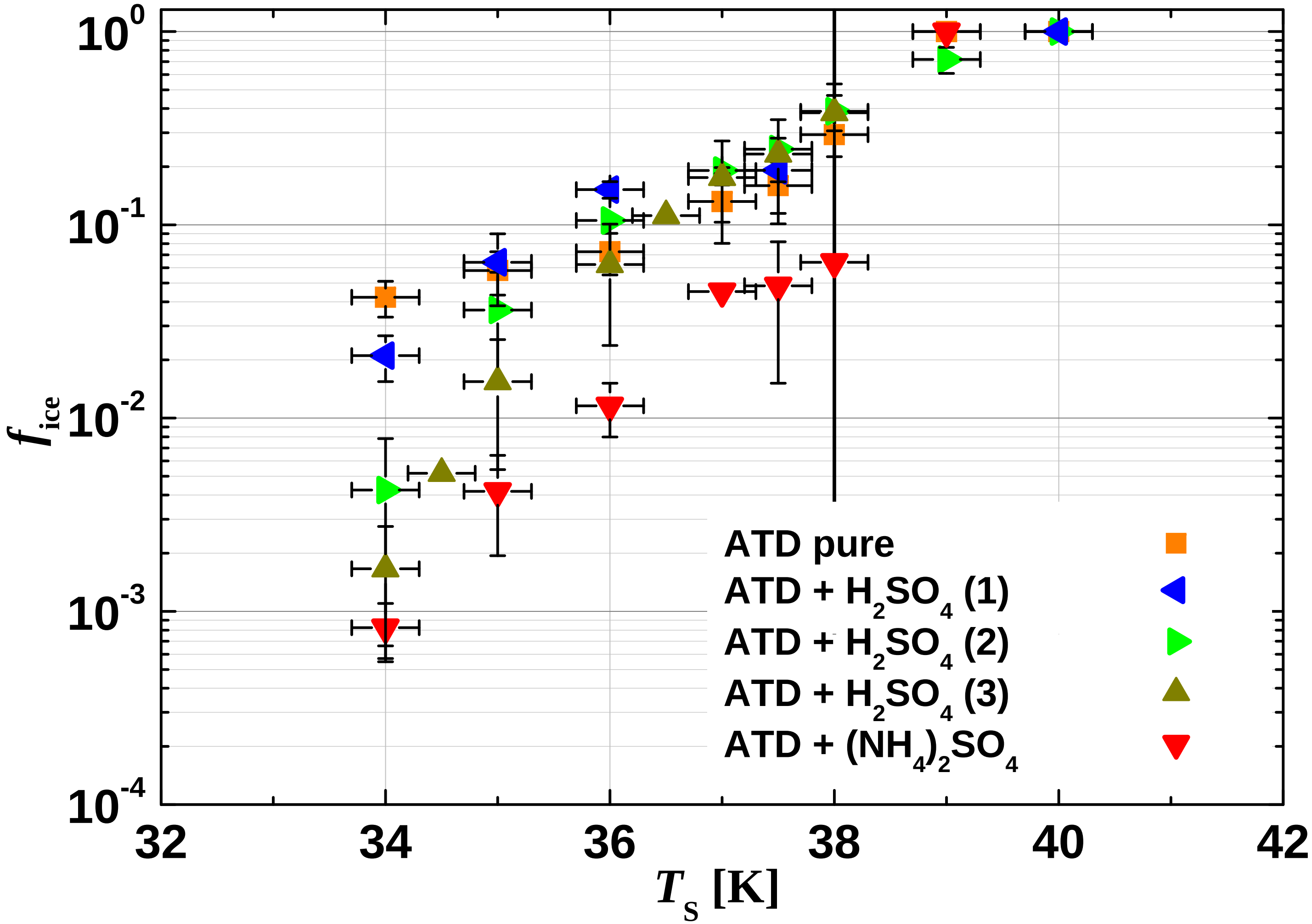
Ice fractions for 300 nm pure ATD particles



Ice fraction for all types of particles



Factors causing the difference in the freezing behavior:

- Water activity dependence? <u>NO!</u>

- Modifications of IN's Surfaces? Most presumable

  → To test this hypothesis two parameterizations based on the stochastic and the singular hypothesis were derived.
  → We may learn which of these two approaches is more suitable in explaining the investigated immersion freezing process.

Stochastic hypothesis

- Based on Classical Nucleation Theory (CNT)
- The IN increases the likelihood to form critical cluster for phase transition
- IN does not disturb the stochastic nature of the freezing process

- Continuous ice nucleation

Singular hypothesis

- Deterministic fashion
- Freezing occurs at characteristic freezing temperature T_c
- T_c specific for each IN/surface site
- The highest T_c determines the freezing temperature of the droplet

- Instantaneous ice nucleation

1. Stochastic Approach

A fit procedure, based on a simplified CNT type nucleation rate expression was performed.

Assumption: constant nucleation rate (constant T_s)

$$j_{\mathrm{het}}(T_{\mathrm{s}}) = a' \times \exp\left(-\frac{C_1\left(1-\frac{T_{\mathrm{s}}}{C_2}\right)^3}{T_{\mathrm{s}}^2} f_{\mathrm{het}}\right) \qquad f_{\mathrm{ice}} = 1 - \exp\left(-s_{\mathrm{p}} j_{\mathrm{het}}(T_{\mathrm{s}}) t\right)$$

$$f_{\mathrm{ice}} = 1 - \exp\left(-a \times \exp\left(-\frac{C_1\left(1-\frac{T_{\mathrm{s}}}{C_2}\right)^3}{T_{\mathrm{s}}^2} f_{\mathrm{het}}\right) t\right) \quad \text{with} \quad a = a' s_{\mathrm{p}}$$

Total surface and Kinetics

Thermodynamics

2. Singular Approach

A fit procedure was performed assuming that ice germ formation takes place on specific sites at a characteristic temperature.

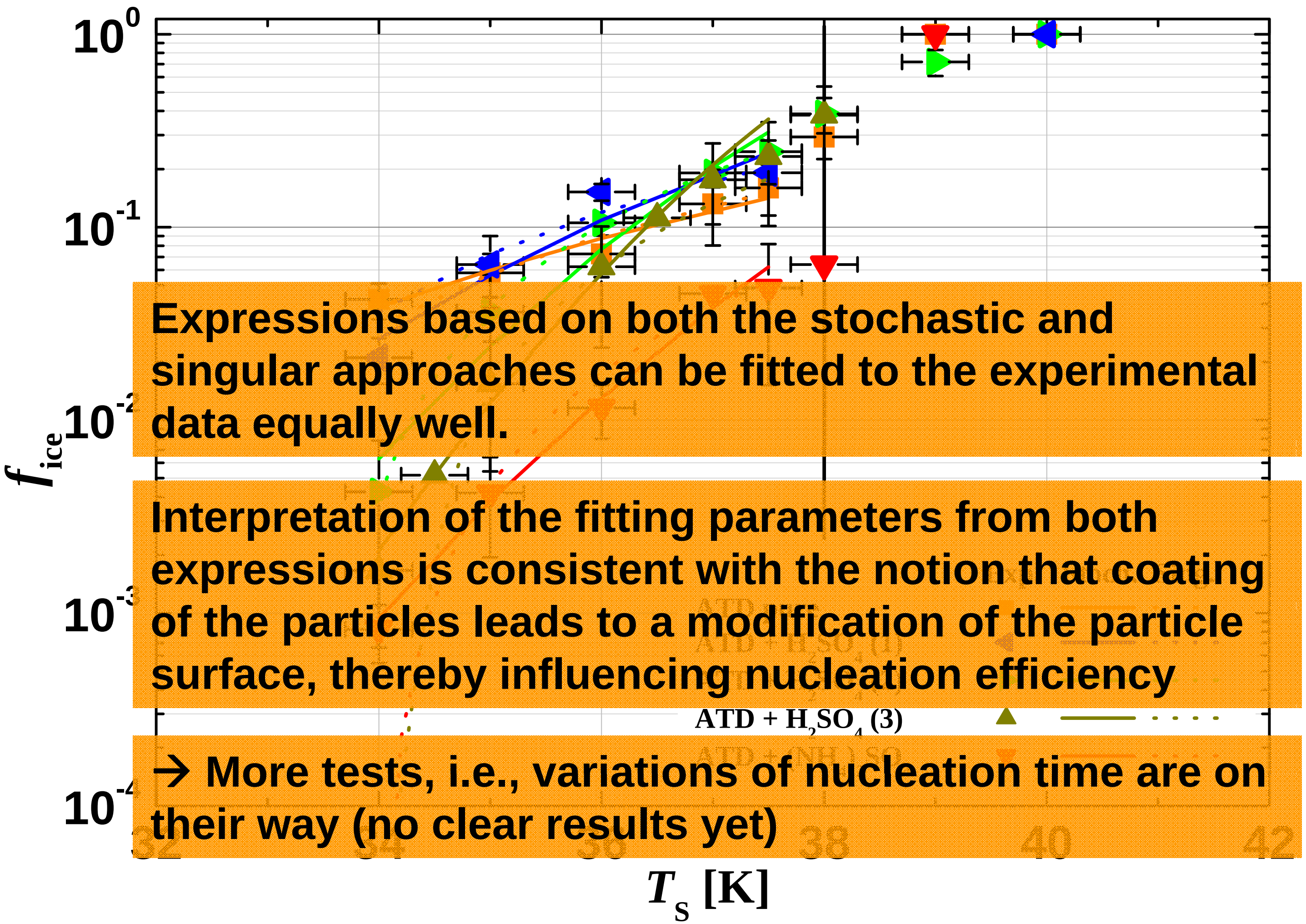
$$f_{ice} = 1 - \exp(-s_p n_s(T))$$

Number of sites per surface area which become ice active between T_0 and T_{min}

For parameterizing $n_s(T)$, a polynomial expression is used as suggested in Connolly et al. (2009):

$$n_s(T) = \begin{cases} \alpha_1 (T + \alpha_2)^2 & T < -\alpha_2 \\ 0 & T \geq -\alpha_2, \end{cases}$$

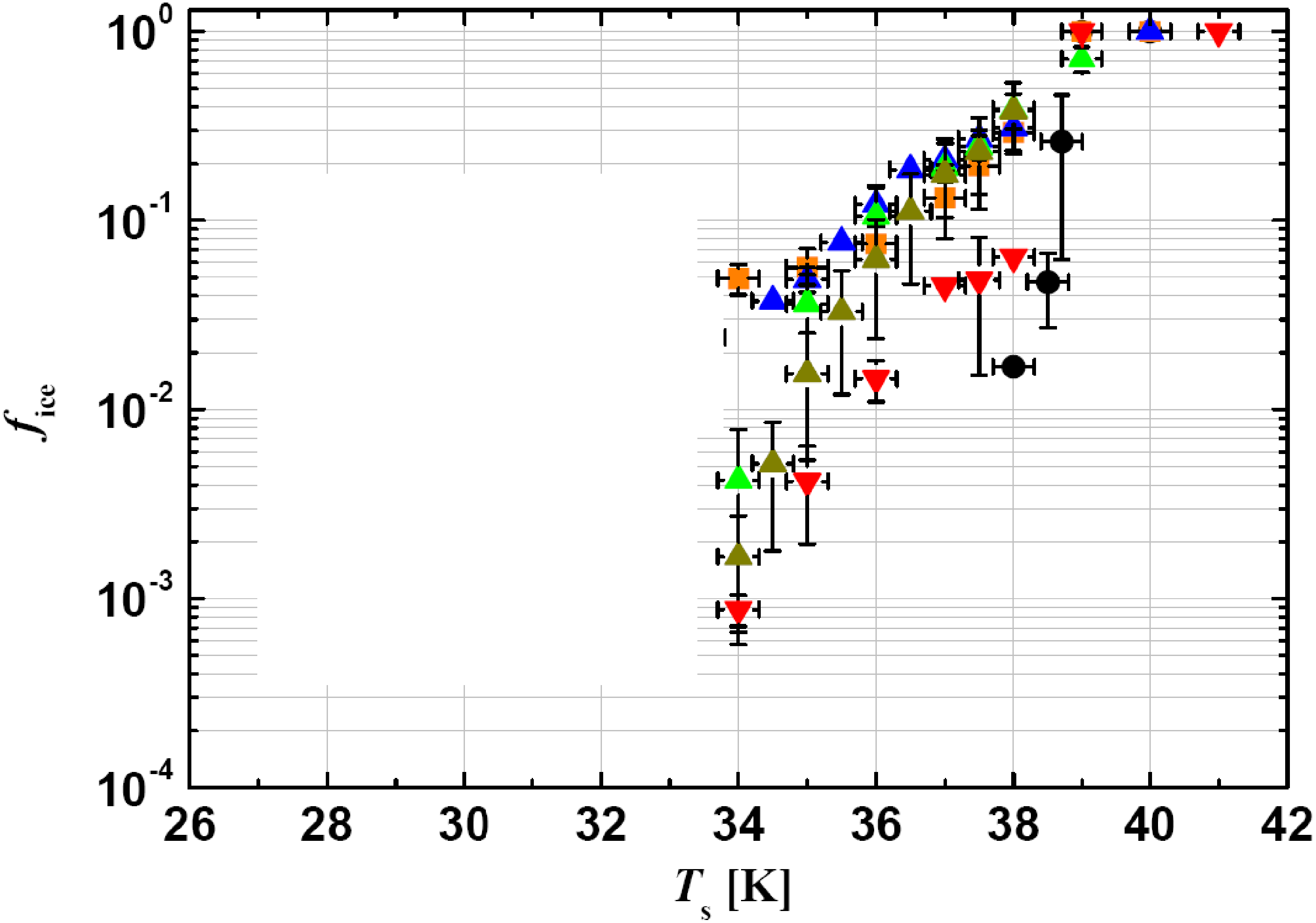
Ice fraction for all types of particles → including fitted curves



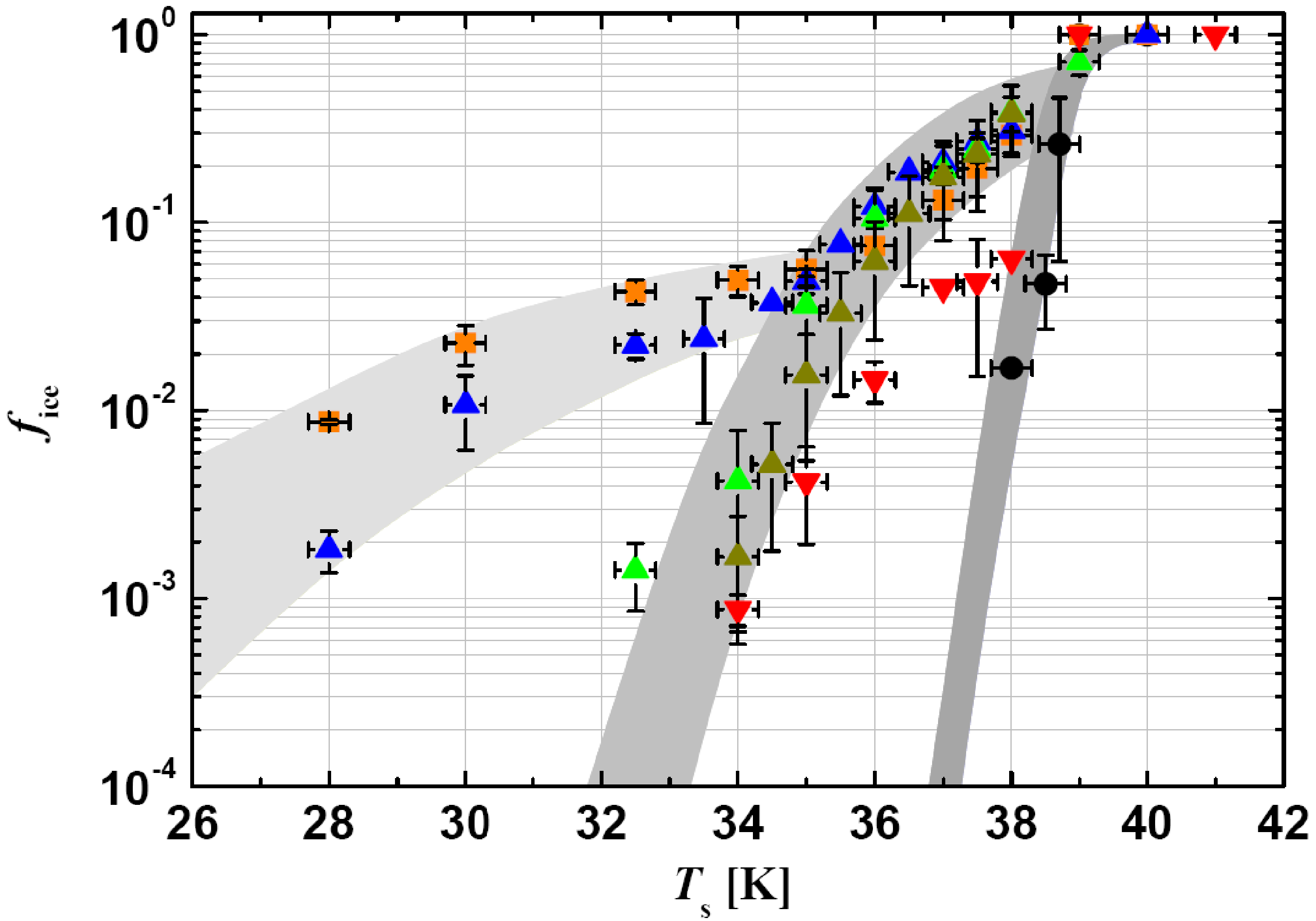
Expressions based on both the stochastic and singular approaches can be fitted to the experimental data equally well.

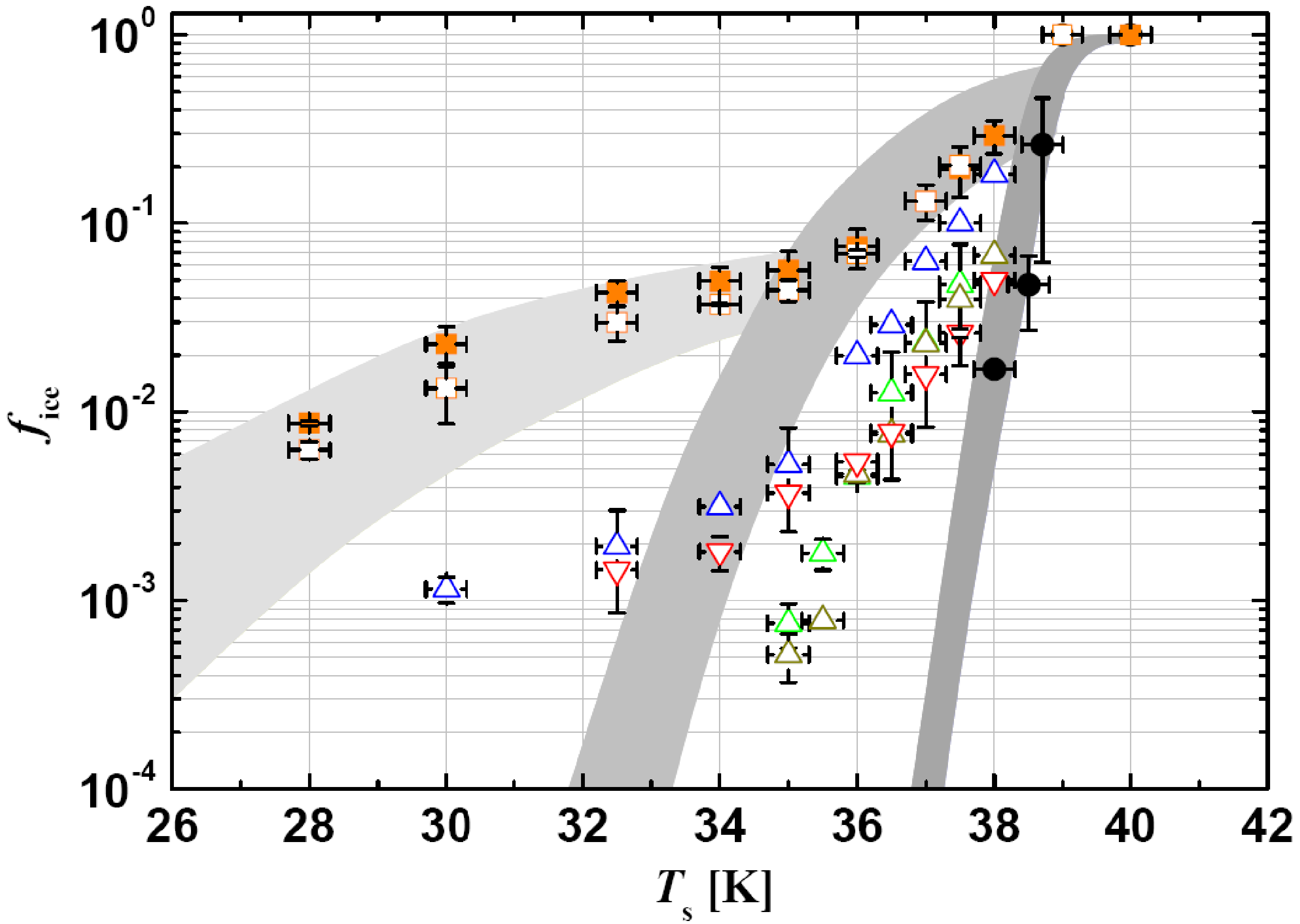
Interpretation of the fitting parameters from both expressions is consistent with the notion that coating of the particles leads to a modification of the particle surface, thereby influencing nucleation efficiency

→ More tests, i.e., variations of nucleation time are on their way (no clear results yet)

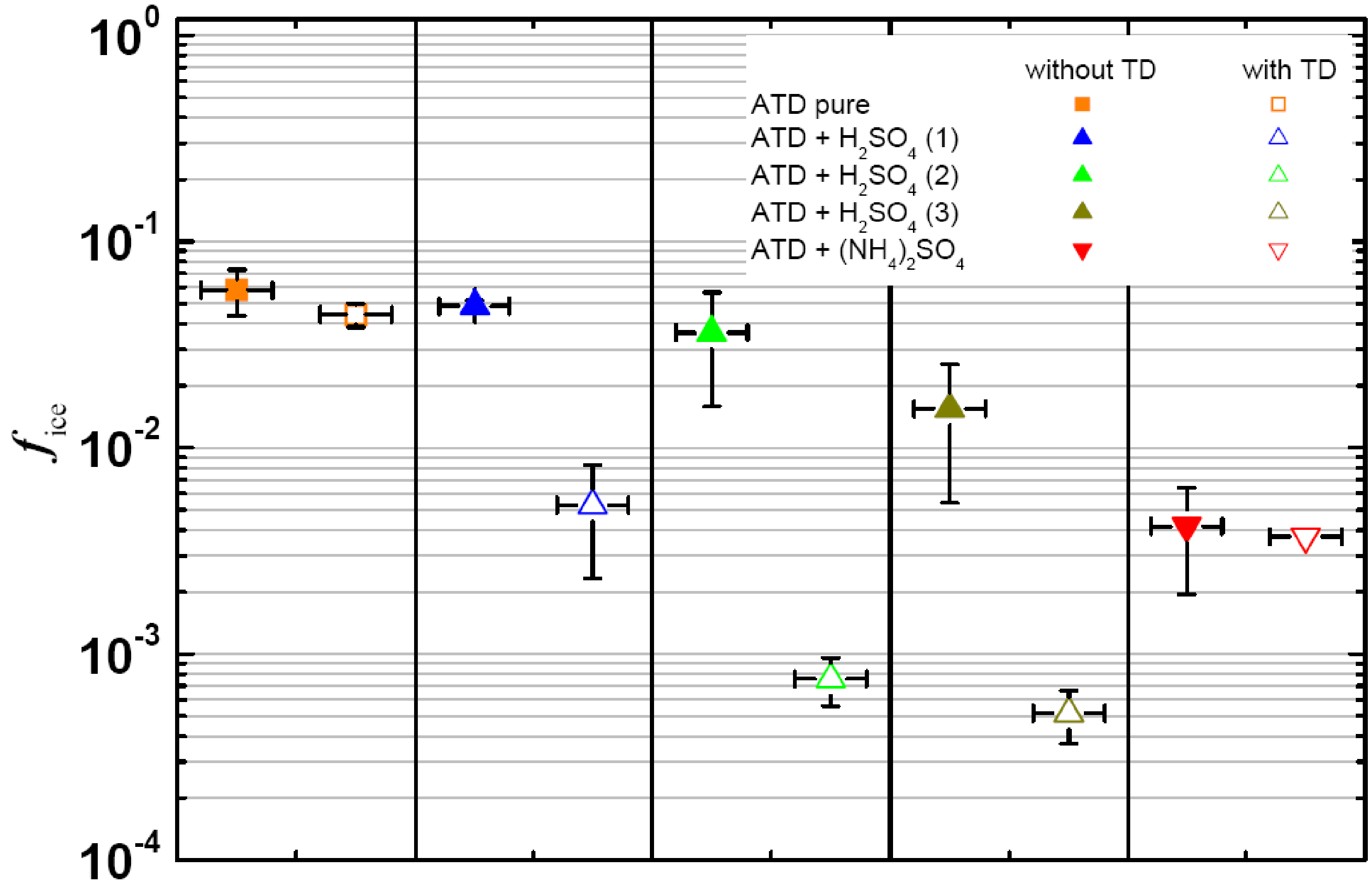


10^0
10^-1
10^-2
10^-3
10^-4
26
28
30
32
34
36
38
40
42
f_ice
T_s [K]


10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
f_{ice}
26
28
30
32
34
36
38
40
42
T_s [K]



10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
f_{ice}
26
28
30
32
34
36
38
40
42
T_s [K]

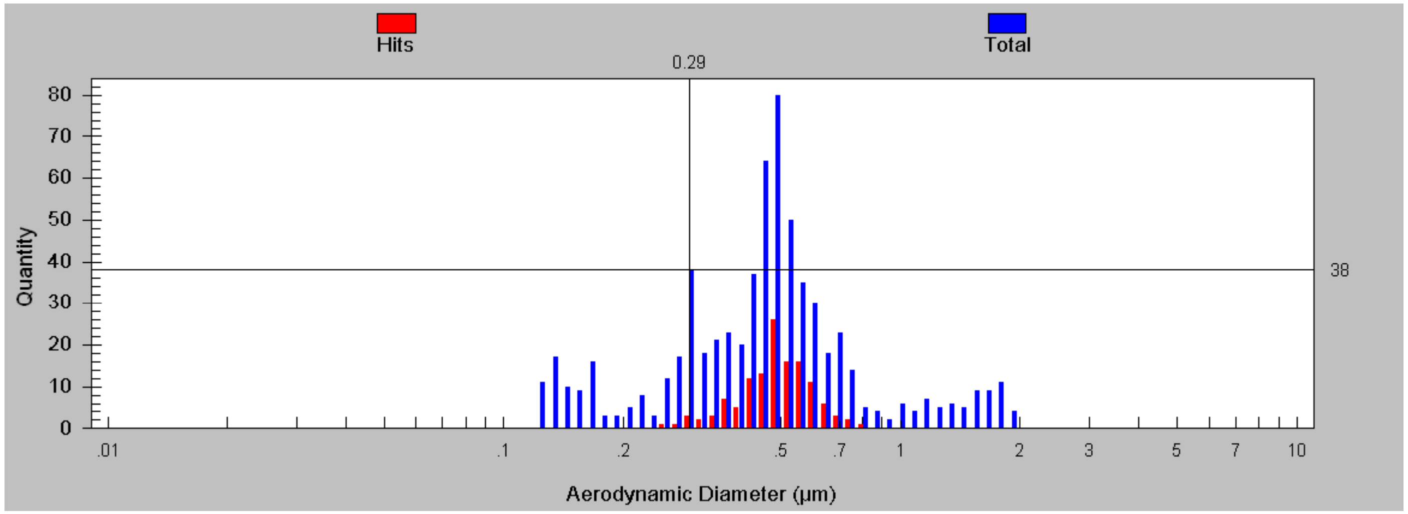


10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
f_{ice}
without TD
with TD
ATD pure
ATD + H_2SO_4 (1)
ATD + H_2SO_4 (2)
ATD + H_2SO_4 (3)
ATD + $(NH_4)_2SO_4$

T_s = 35K

In the immersion freezing regime it seems that two different freezing mechanism/processes occur → Possible explanation:

- The pure ATD particles could consists of two external mixed particle populations (suggested by ATOFMS measurements) where each population features on type of specific sites on the particle surface → Due to coating procedure one population becomes ineffective



Exp 23, 300nm ATD, H_2SO_4 coated, w/ Thermodenuder

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- Influence of different coatings and thermal treatment on freezing behavior of dust particles (D_{mob} = 300nm) was investigated.

- All coating procedures did not enhance the IN efficiency compared to pure ATD particles → In most cases IN ability is decreased.

- In general, thermodenuder decreases the IN ability even further (apart from pure ATD and ammonium sulfate coating).

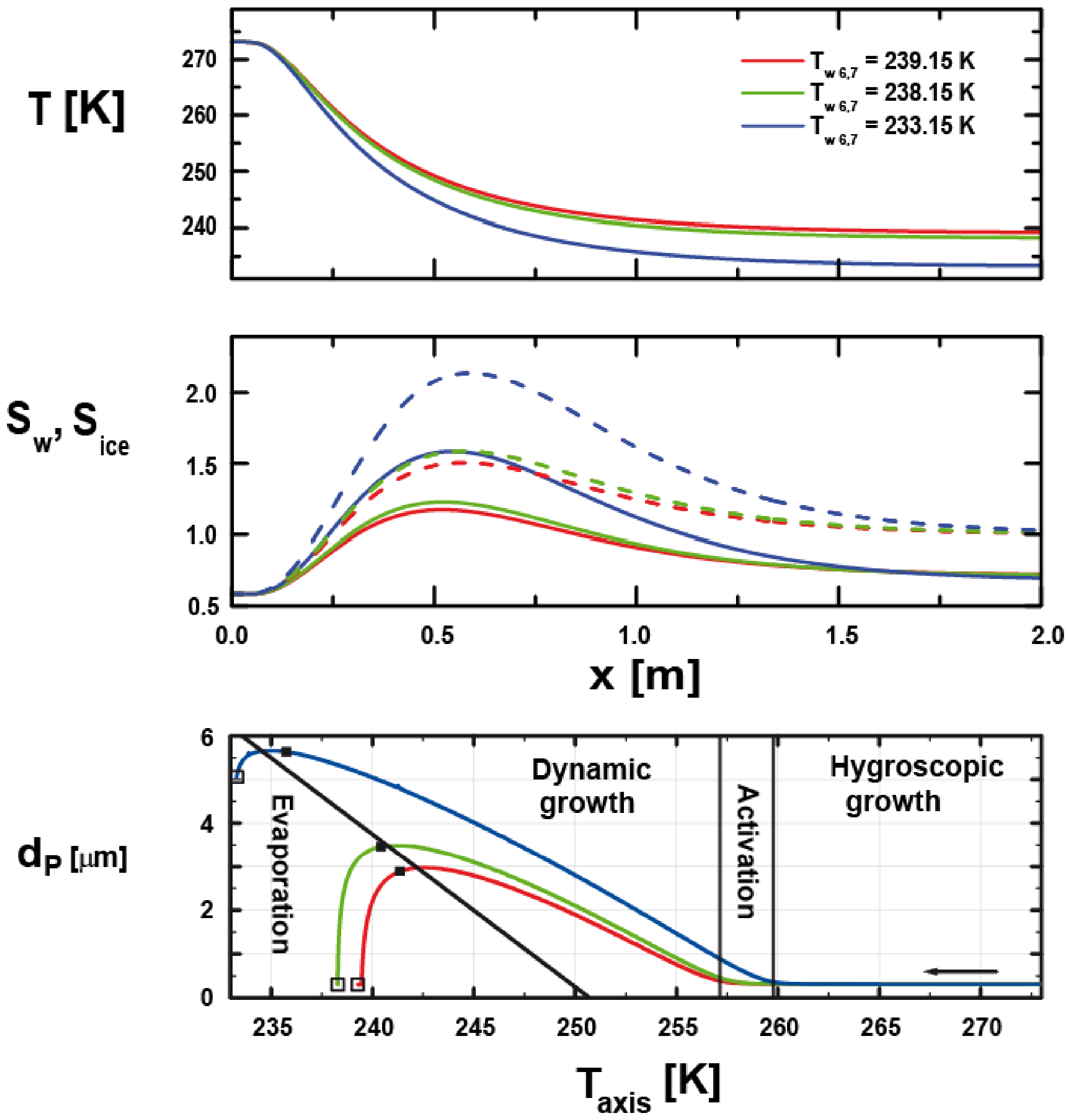
- Freezing point suppression due to the soluble material on the particles (and therefore in the droplets) can not explain the observations because the supercooled droplets were highly diluted before freezing occurred.

- Freezing behavior differences are caused by changes of IN's surface due to the coatings. → Parameterizations based on stochastic and singular hypothesis confirm this finding.

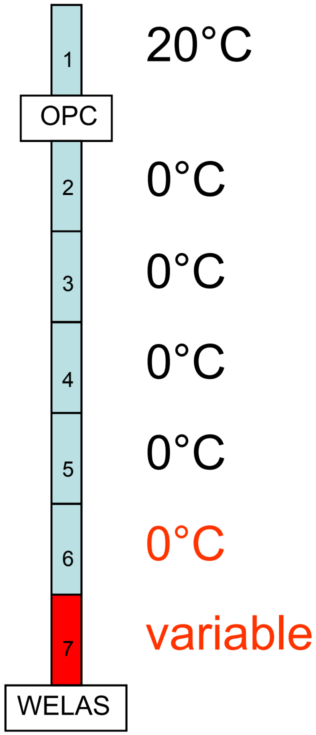
- More strenuous tests, including different aerosol types and temperature ranges, and especially variations in nucleation time have to be performed in order to clearly favor one interpretation over the other.

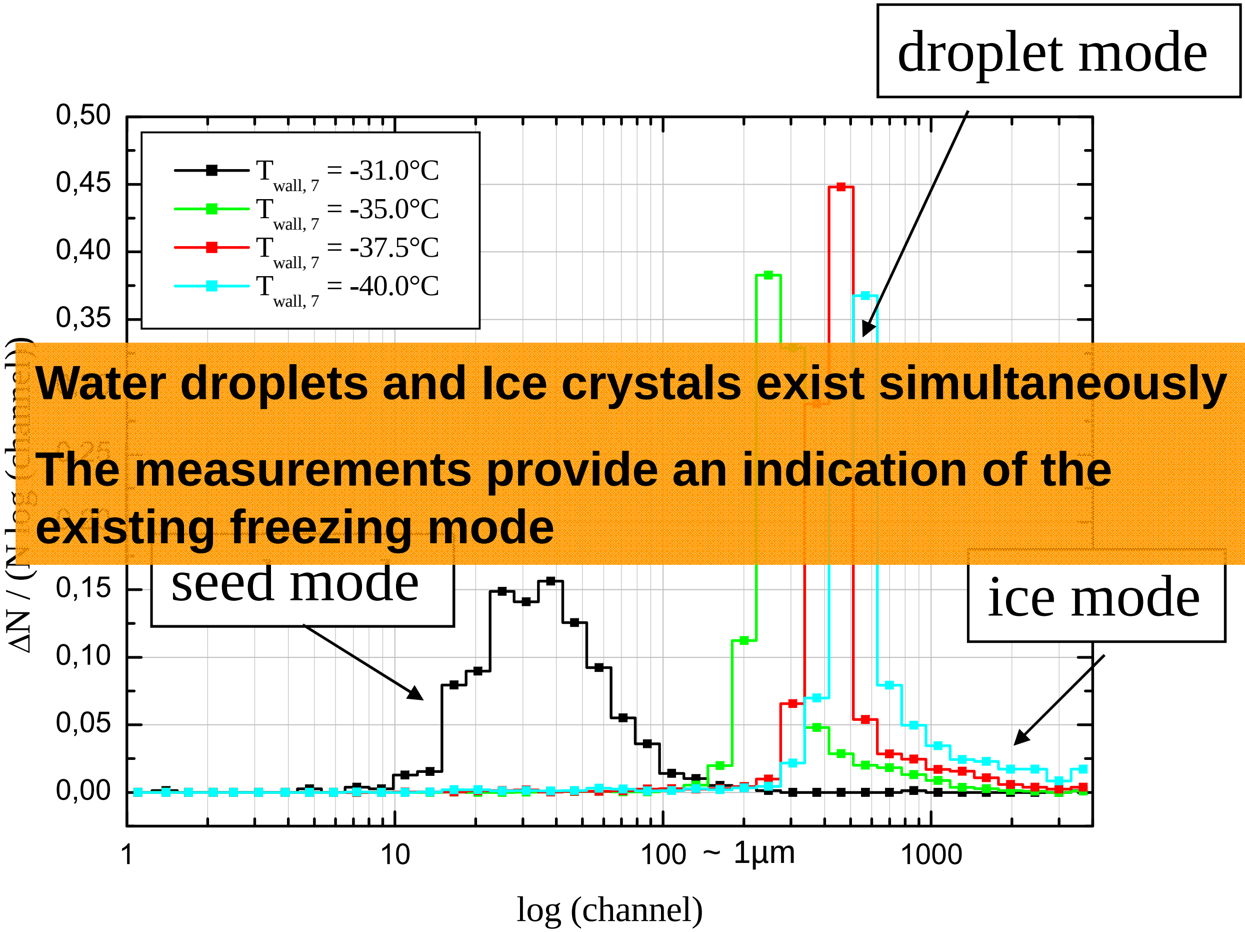
- BET analysis of treated and untreated ATD particle samples to get information whether total particle surface has changed.

- EDS analysis for chemical composition of individual particle samples (treated and untreated ATD).


T [K]
270
260
250
240
$T_{w\,6,7}$ = 239.15 K
$T_{w\,6,7}$ = 238.15 K
$T_{w\,6,7}$ = 233.15 K
S_w, S_{ice}
2.0
1.5
1.0
0.5
0.0
0.5
1.0
1.5
2.0
x [m]
d_P [μm]
6
4
2
0
Evaporation
Dynamic growth
Activation
Hygroscopic growth
235
240
245
250
255
260
265
270
T_{axis} [K]

One-section measurement

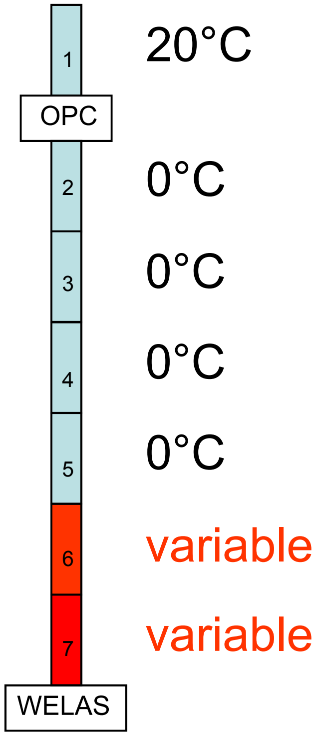


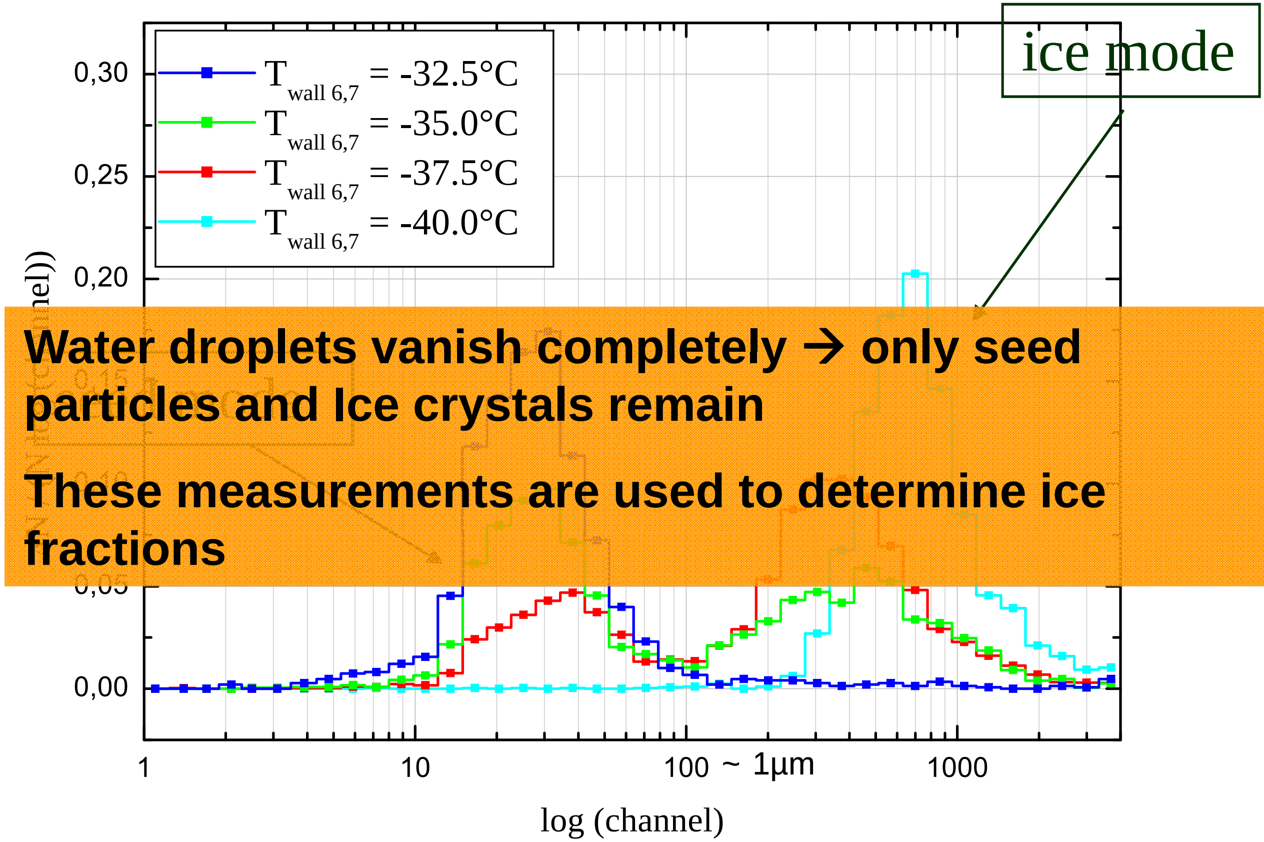


Water droplets and Ice crystals exist simultaneously

The measurements provide an indication of the existing freezing mode

Two-section measurement





Water droplets vanish completely → only seed particles and Ice crystals remain

These measurements are used to determine ice fractions

- Pure ATD particles
  - Pure ATD particles are the most efficient IN
  - Thermodenuder does not change IN ability

- H_2SO_4 coatings
  - IN capability decreases with increasing coating temperature
    → Reaction of sulfuric acid and ATD particle
  - Thermodenuder leads to a further decreased IN ability
    → Further surface changes due to increased reaction on particle surface caused by the heating

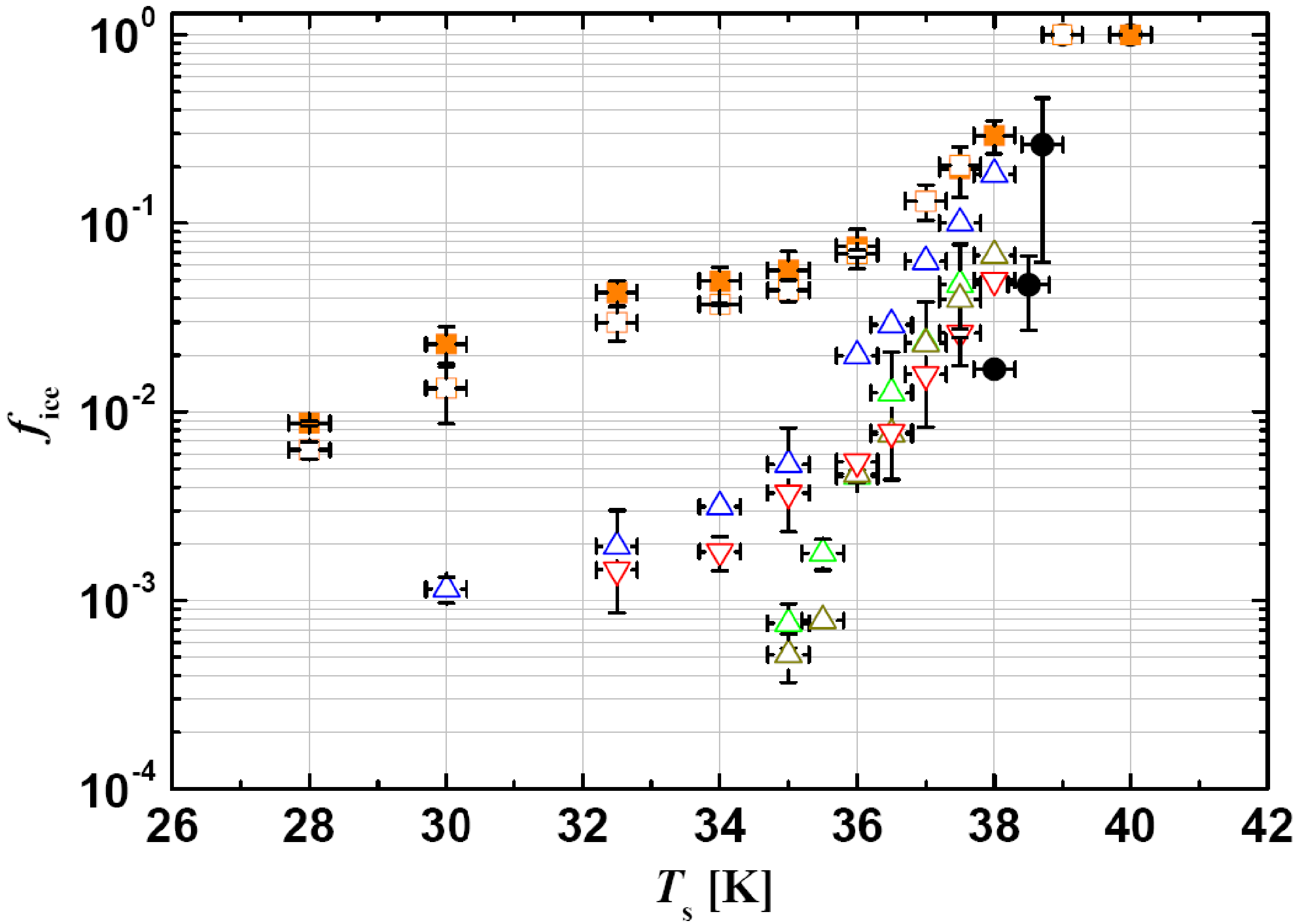
- $(NH_4)_2SO_4$ coatings
  - Exposure of H_2SO_4 to water vapor accelerates the reaction with the mineral dust, leading to the greatest reduction in nucleating efficiency
  - Small differences between measurements with and without Thermodenuder
  - Thermodenuder increases IN ability slightly for $T_s \leq 32.5K$

Stochastic | Singular

Particle Type	a [s^{-1}]	f_{het}	α_1 [m^{-2}°C^{-2}]	α_2 [°C]
ATD	1.31E+00	4.51E-02	1.50925E+10	31.29
ATD + $C_4H_6O_4$	8.46E+00	6.83E-02	2.01066E+10	31.66
ATD + H_2SO_4 (1)	1.57E+01	7.79E-02	2.37200E+10	31.65
ATD + H_2SO_4 (2)	5.71E+02	1.35E-01	6.32827E+10	33.54
ATD + H_2SO_4 (3)	8.22E+03	1.78E-01	5.77985E+10	34.03
ATD + $(NH_4)_2SO_4$	1.31E+02	1.40E-01	1.52053E+10	33.97

Thermodynamic term seems to be most dominant for the change in immersion freezing behavior investigated

Highest characteristic temperature decreases due to coatings



10^0
10^-1
10^-2
10^-3
10^-4
f_ice
26
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38
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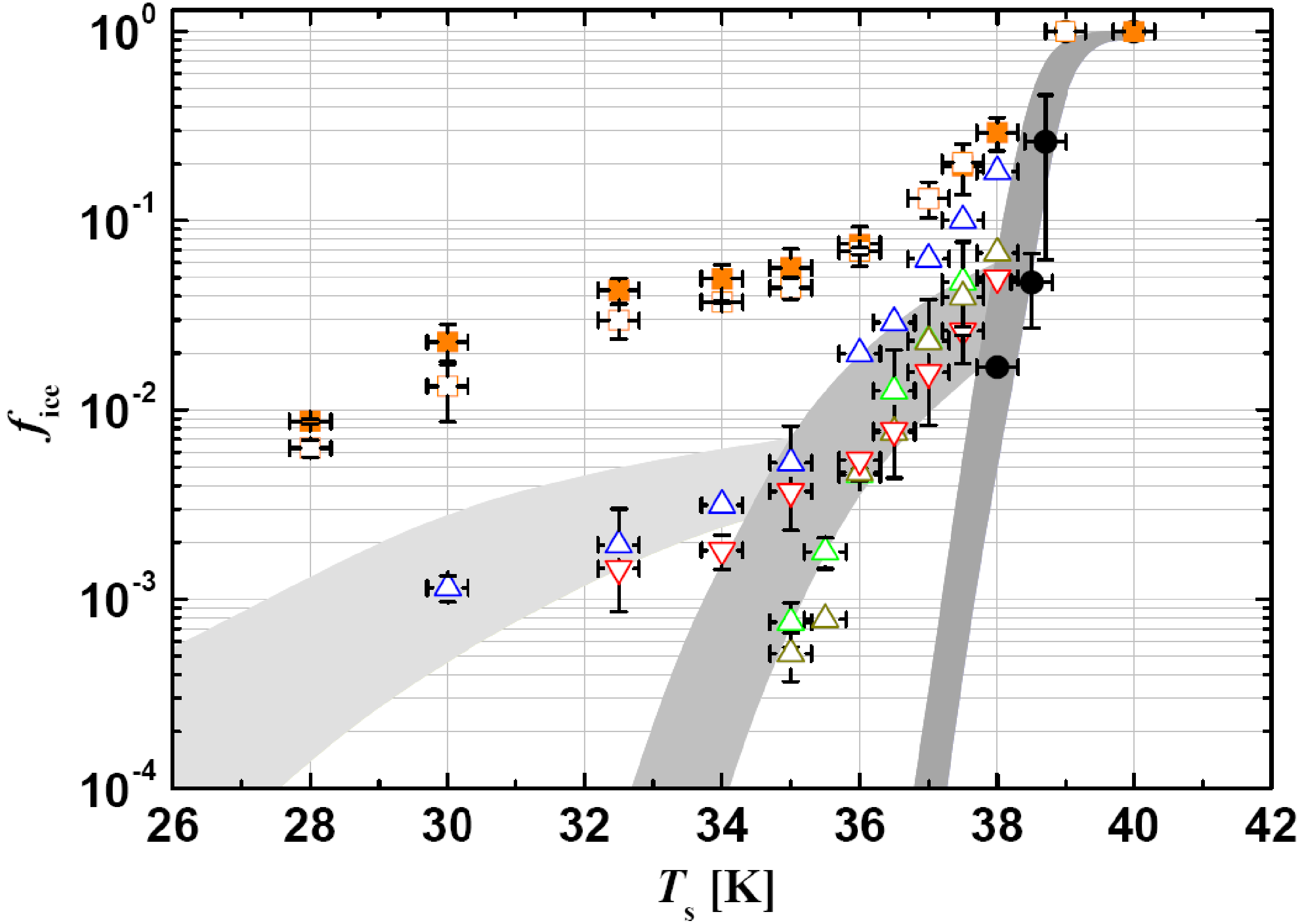
42
T_s [K]



10^0
10^-1
10^-2
10^-3
10^-4
f_ice
26
28
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36
38
40
42
T_s [K]