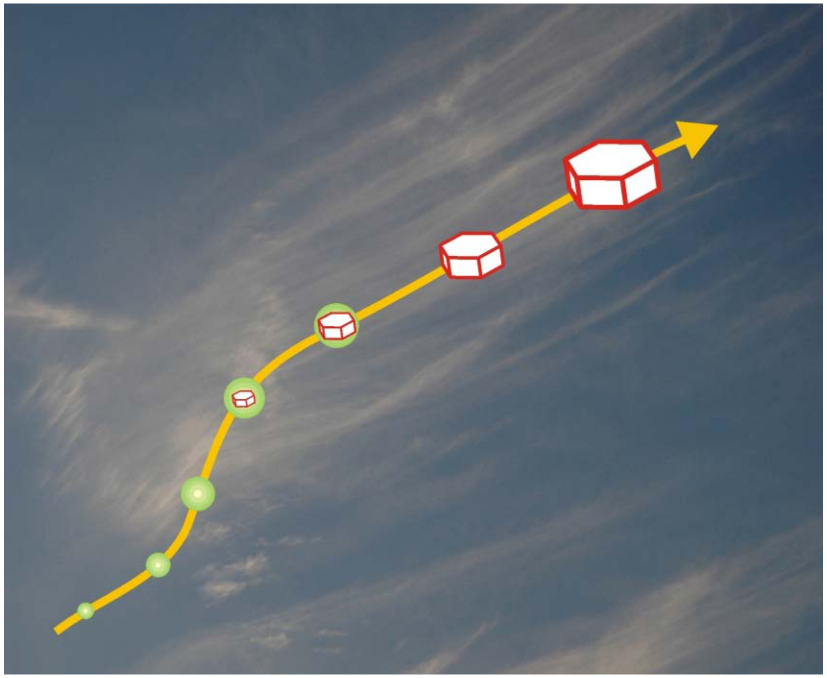
Atmospheric Water Vapor, Aerosols, and Clouds: A Microphysical Perspective



Thomas Koop
Department of Chemistry, Bielefeld University, Germany

with contributions from
Beni Zobrist, Claudia Marcolli, Analia Pedernera, Tom Peter, Ottmar Möhler

SCOUT-O3

4th SPARC General Assembly 2008, Bologna

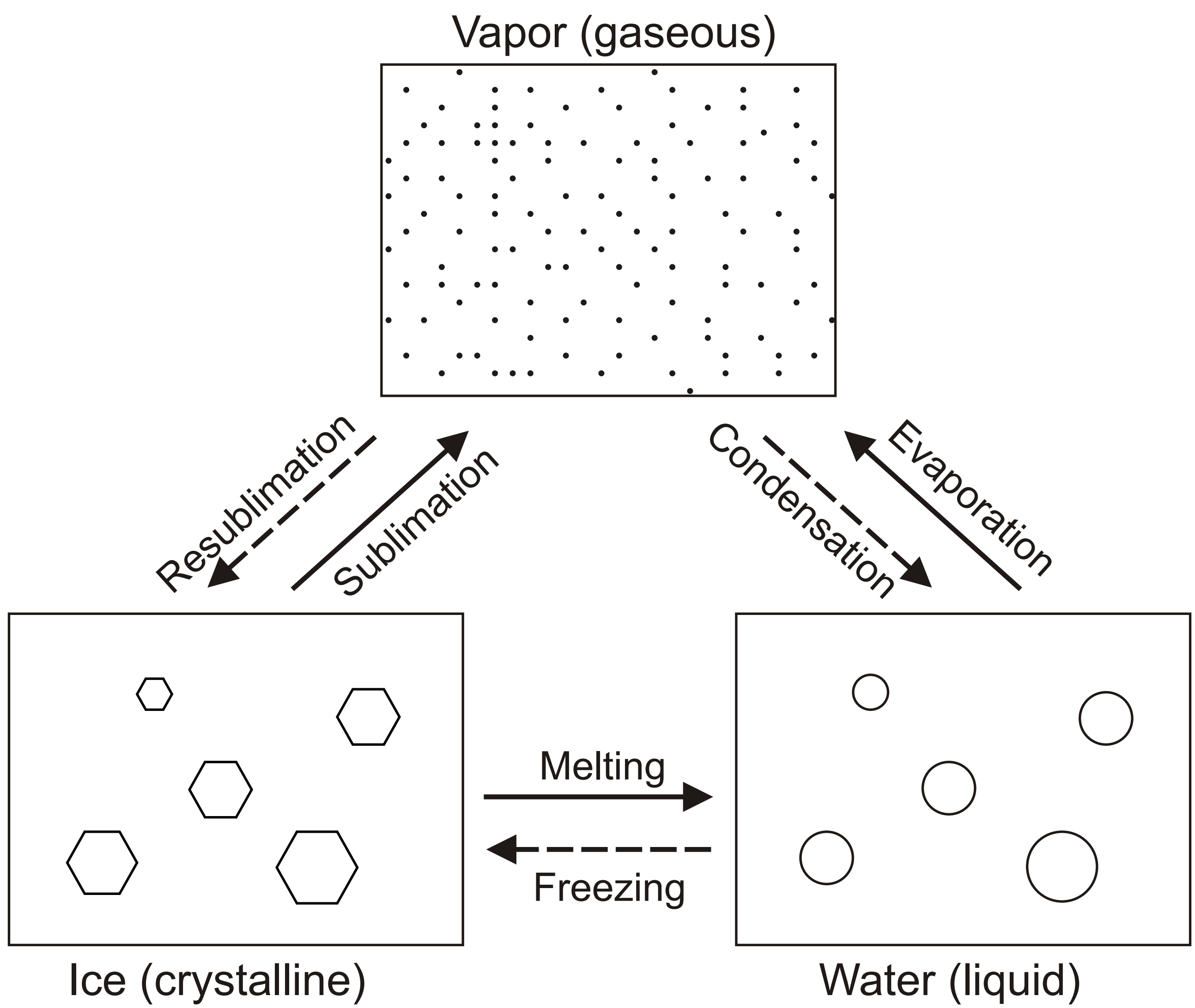
Ice clouds

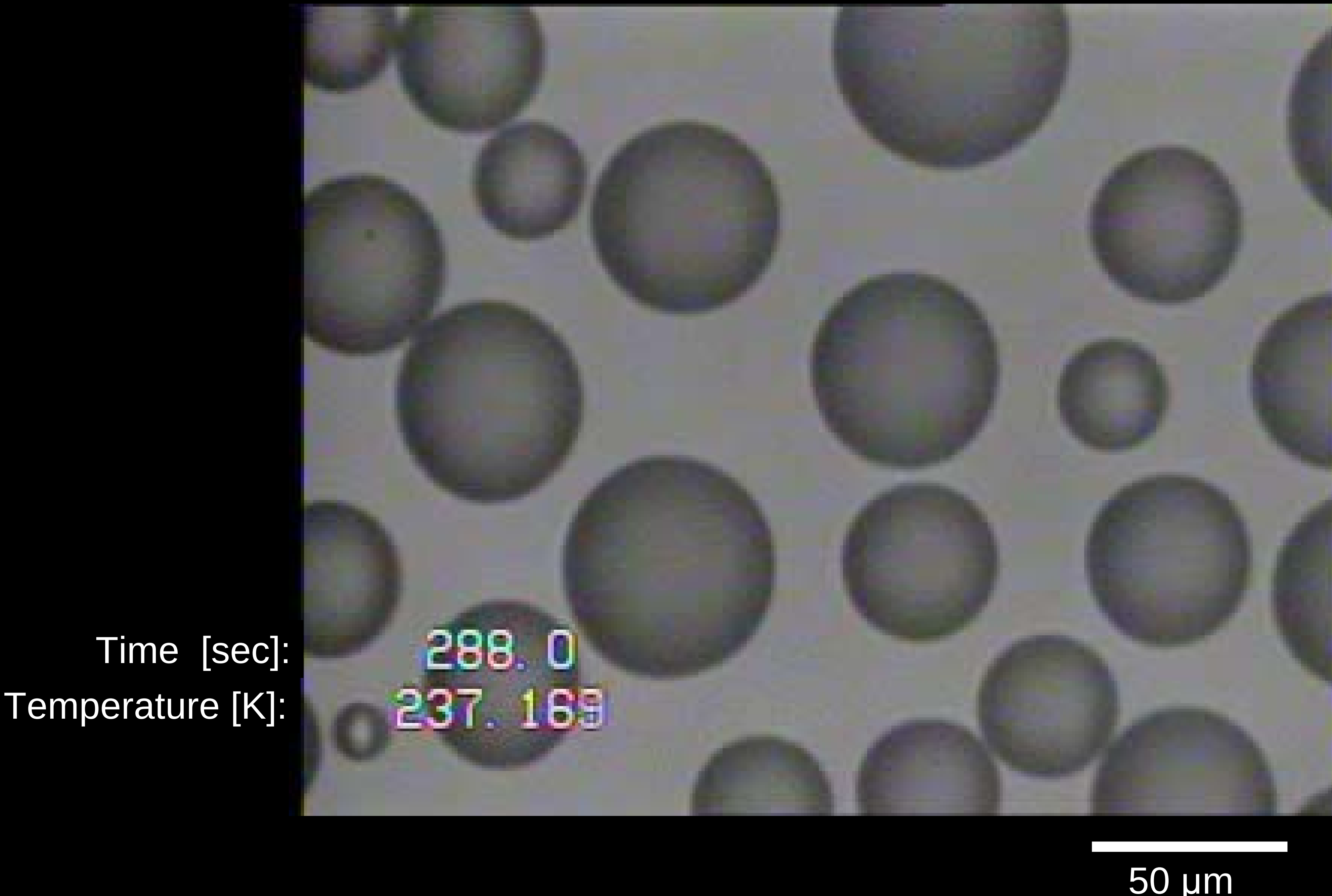
cirrus clouds

~7–17 km

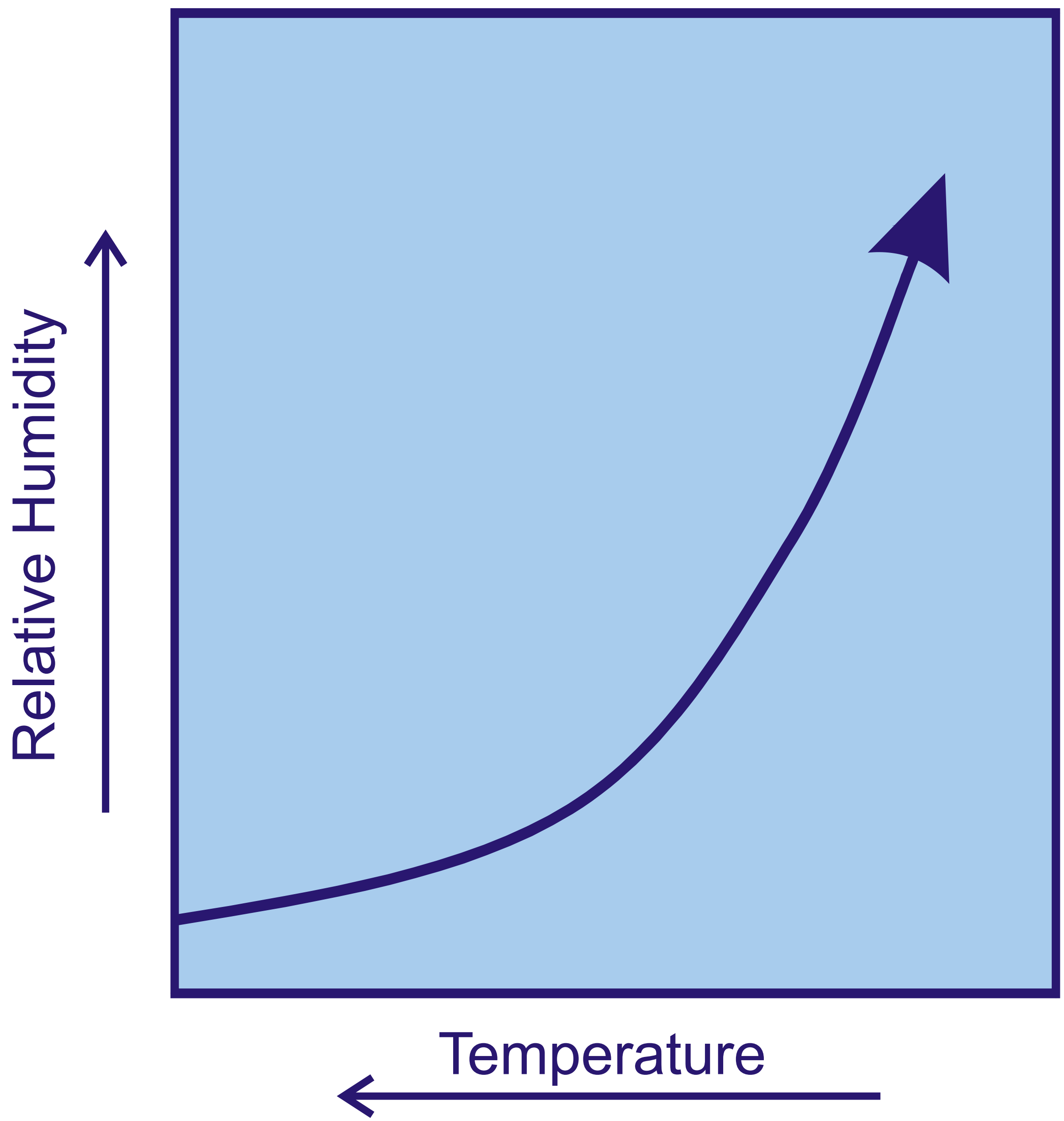
~20–25 km

Polar
Stratospheric Clouds

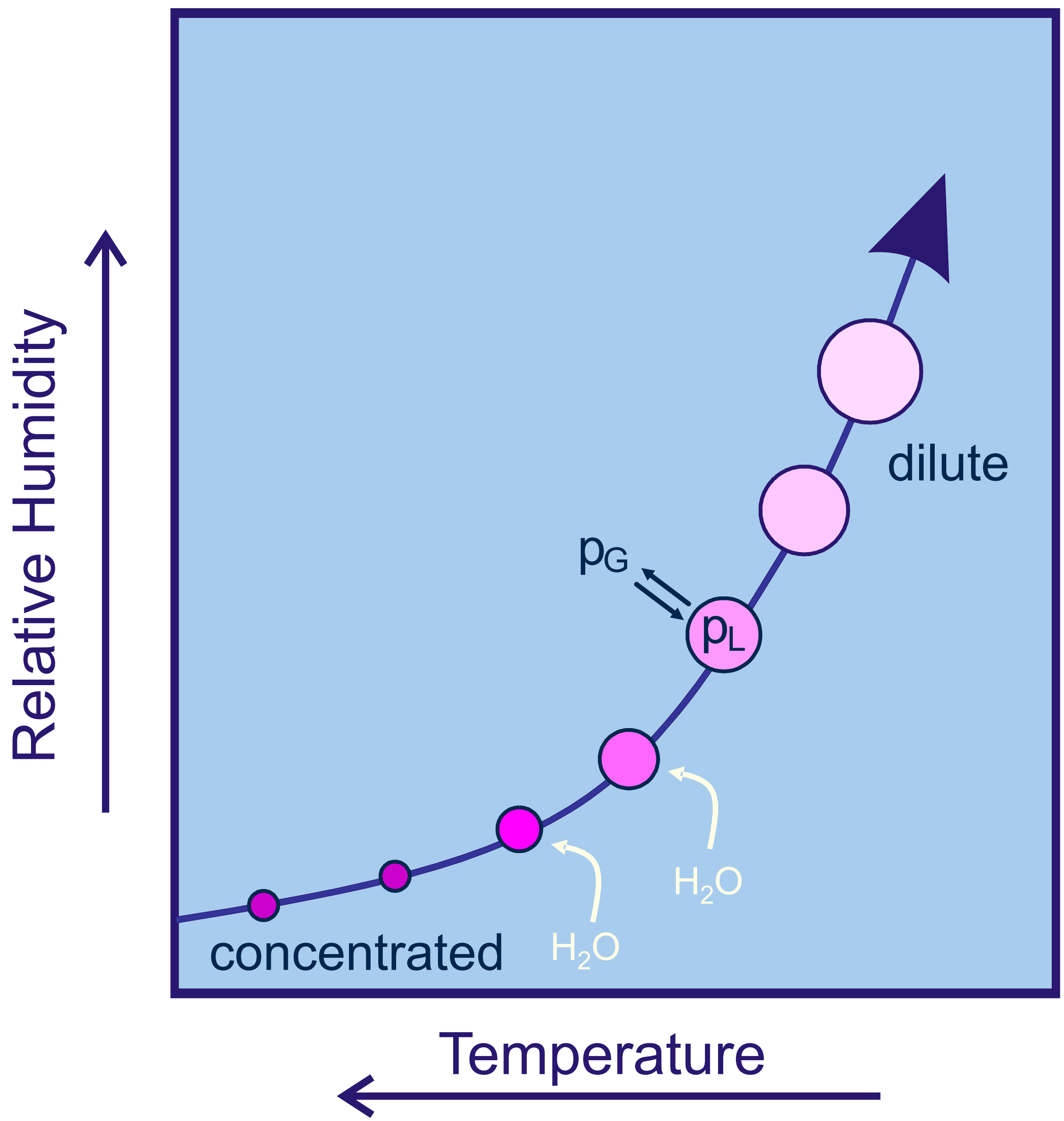

Vapor (gaseous)
Resublimation
Sublimation
Condensation
Evaporation
Melting
Freezing
Ice (crystalline)
Water (liquid)


Time [sec]:
288.0
Temperature [K]:
237.169
50 µm

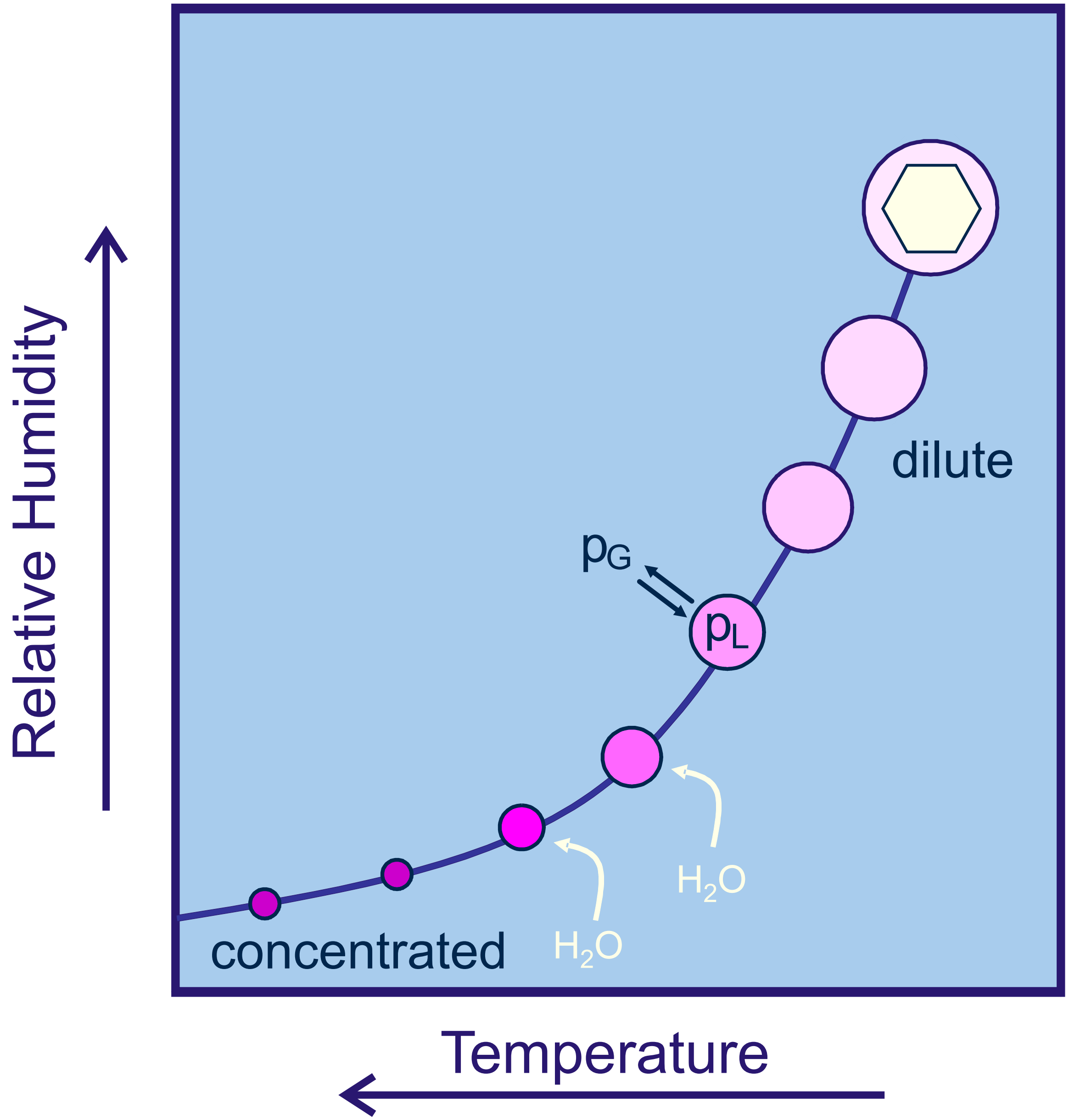
Ice Nucleation in Rising Air Parcel



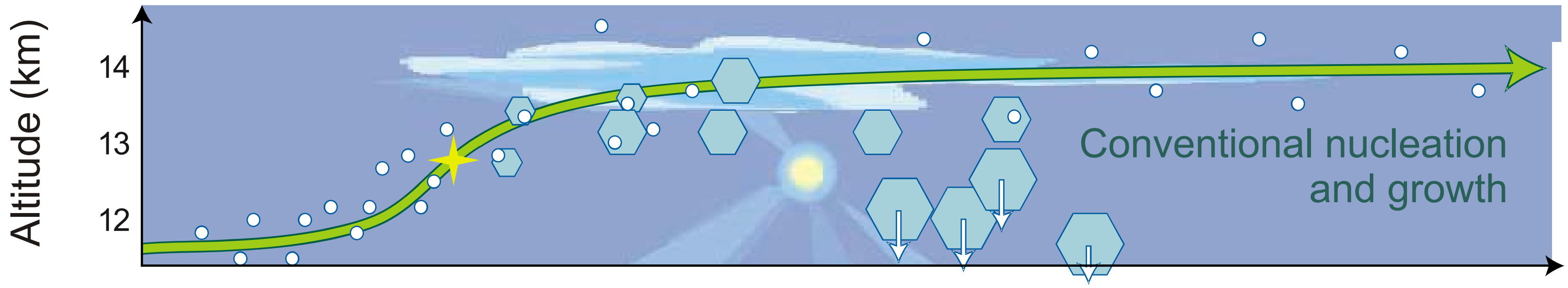
Ice Nucleation in Rising Air Parcel



Ice Nucleation in Rising Air Parcel

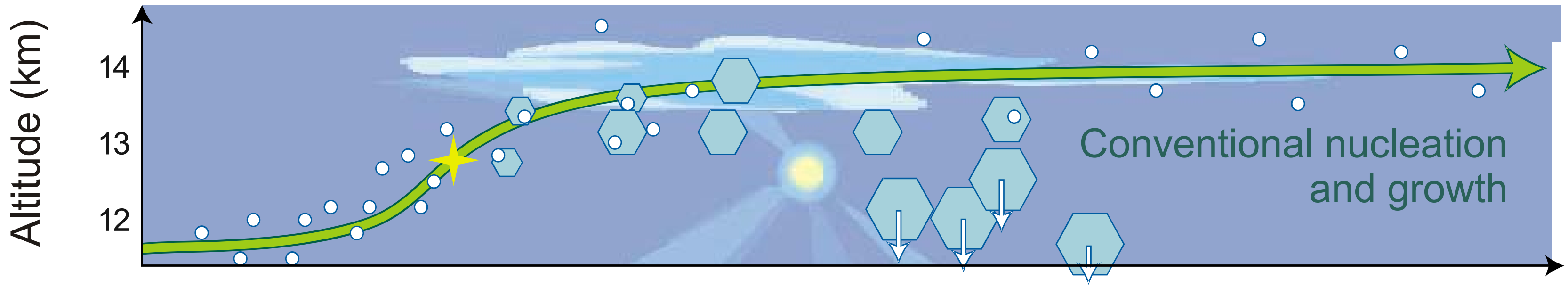


the base case



Peter, Marcolli, Spichtinger, Corti, Baker, Koop, Science 2006

the base case



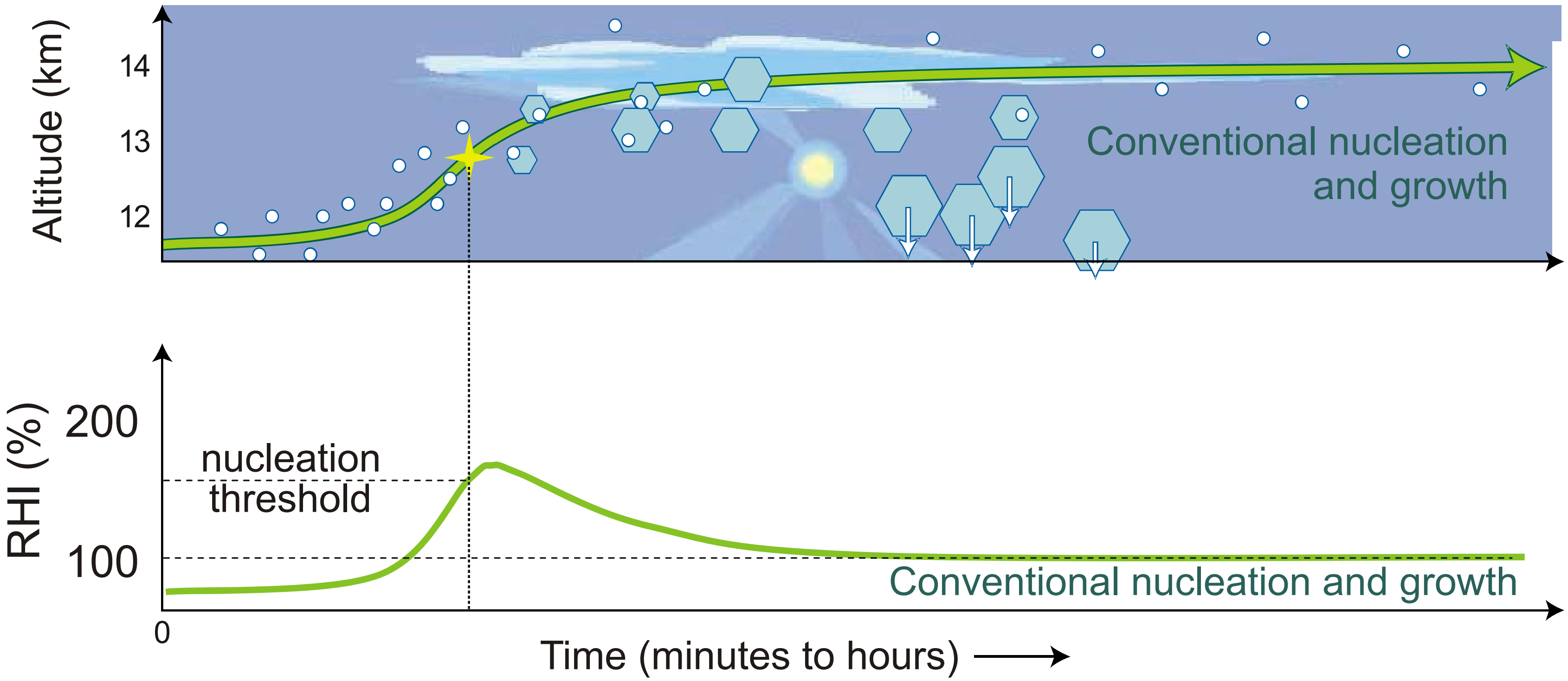
RHI > 100% => ice particles grow

RHI = 100% => ice particles are in equilibrium

RHI < 100% => ice evaporate

Peter, Marcolli, Spichtinger, Corti, Baker, Koop, Science 2006

the base case



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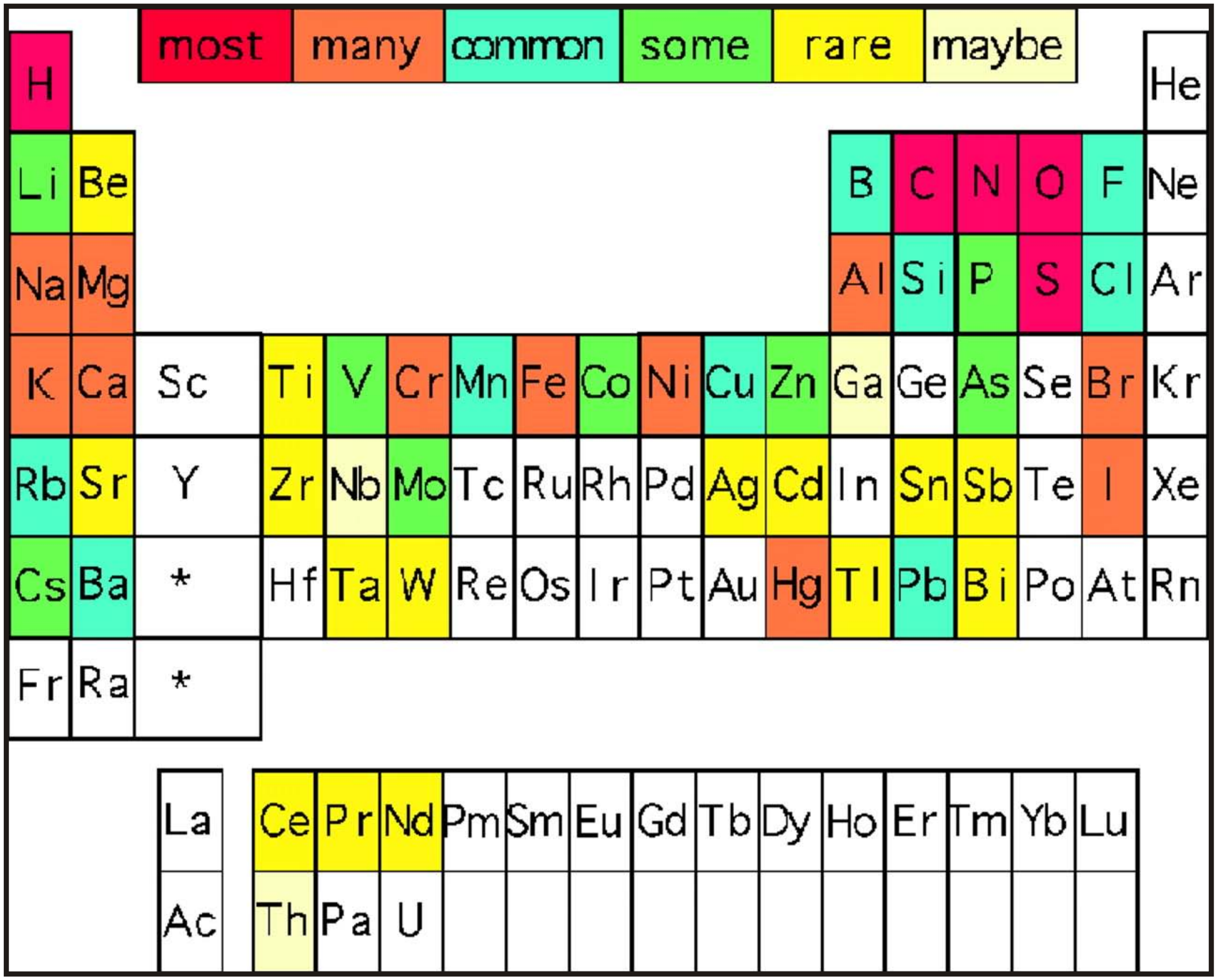
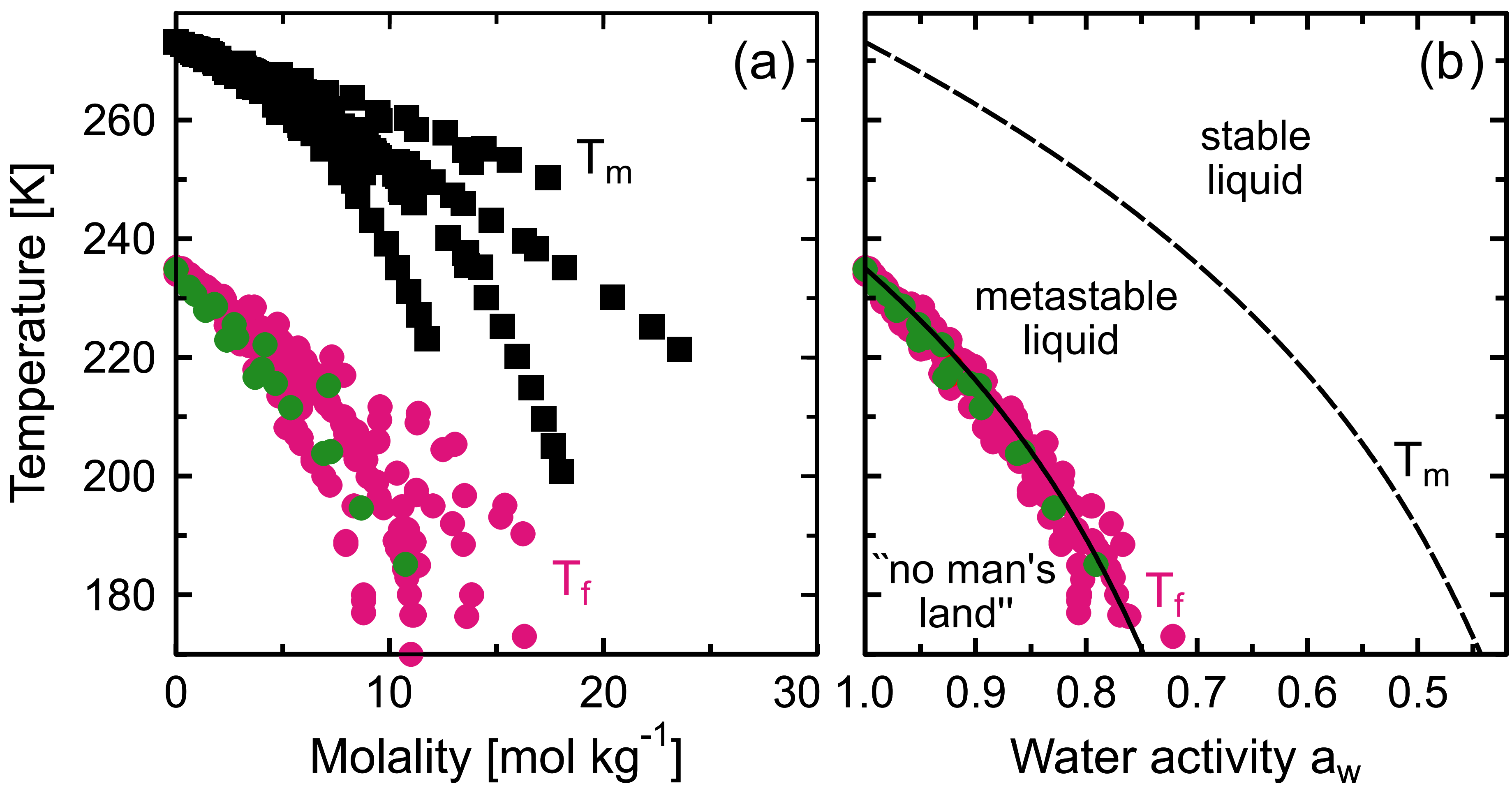
Peter, Marcolli, Spichtinger, Corti, Baker, Koop, Science 2006

Single Aerosol Particle Mass Spectrometry



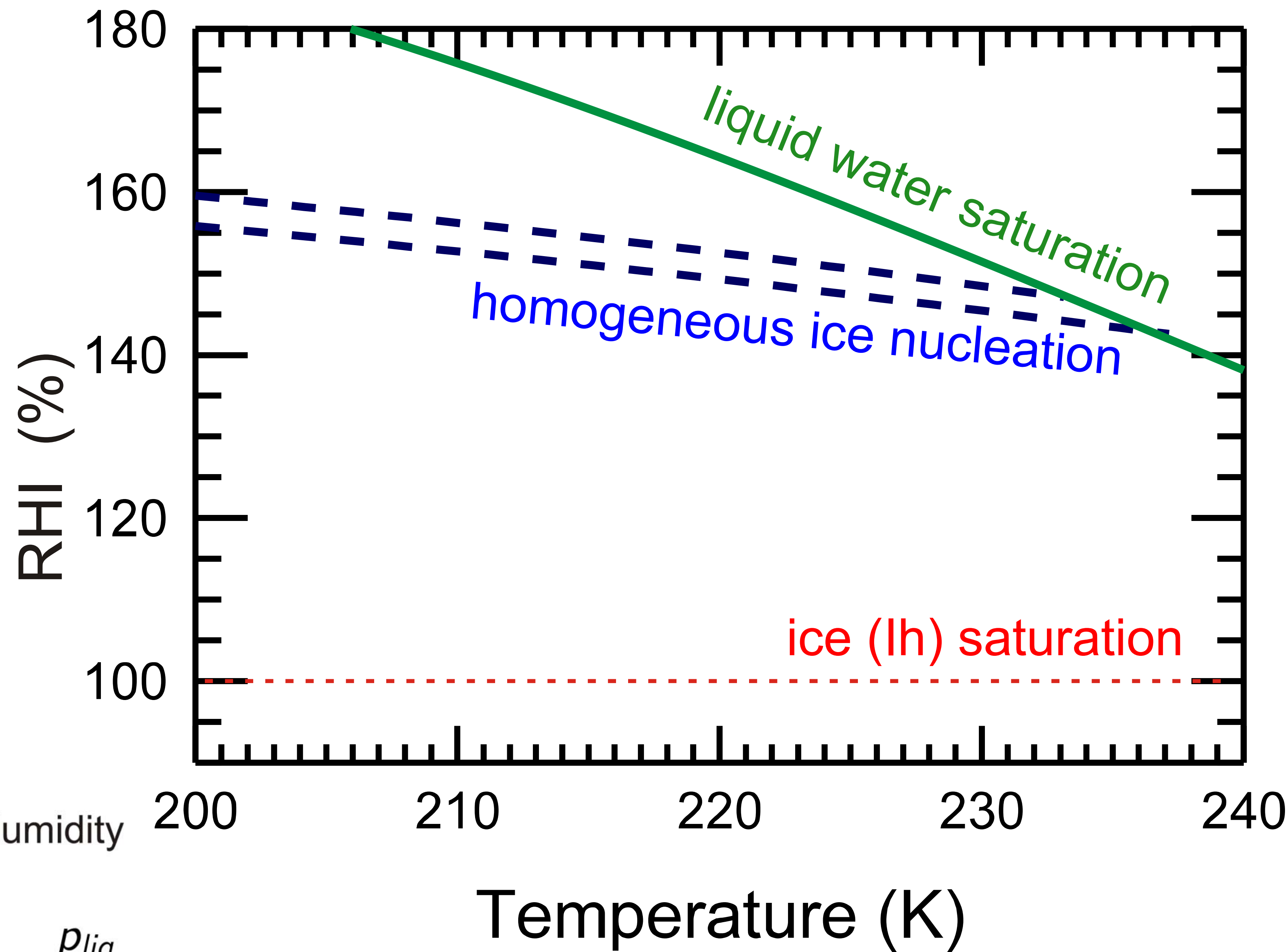
Murphy et al., Science, 1998

Homogeneous Ice Nucleation in Aqueous Solution Droplets



$$a_W \equiv \frac{p_L}{p_{L0}} \overset{eq}{=} \frac{p_G}{p_{L0}} \equiv RH$$

Koop et al., Nature 2000

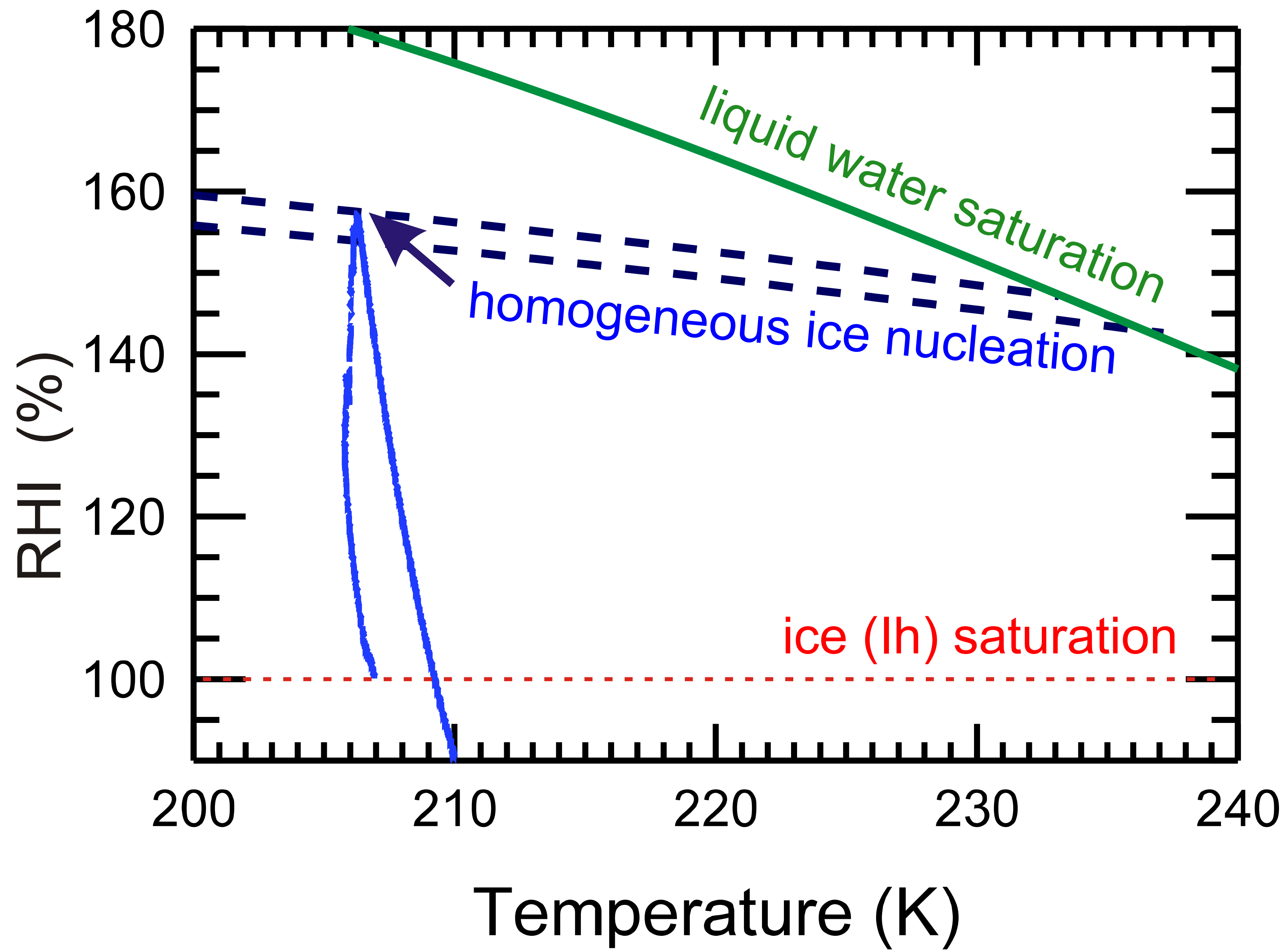


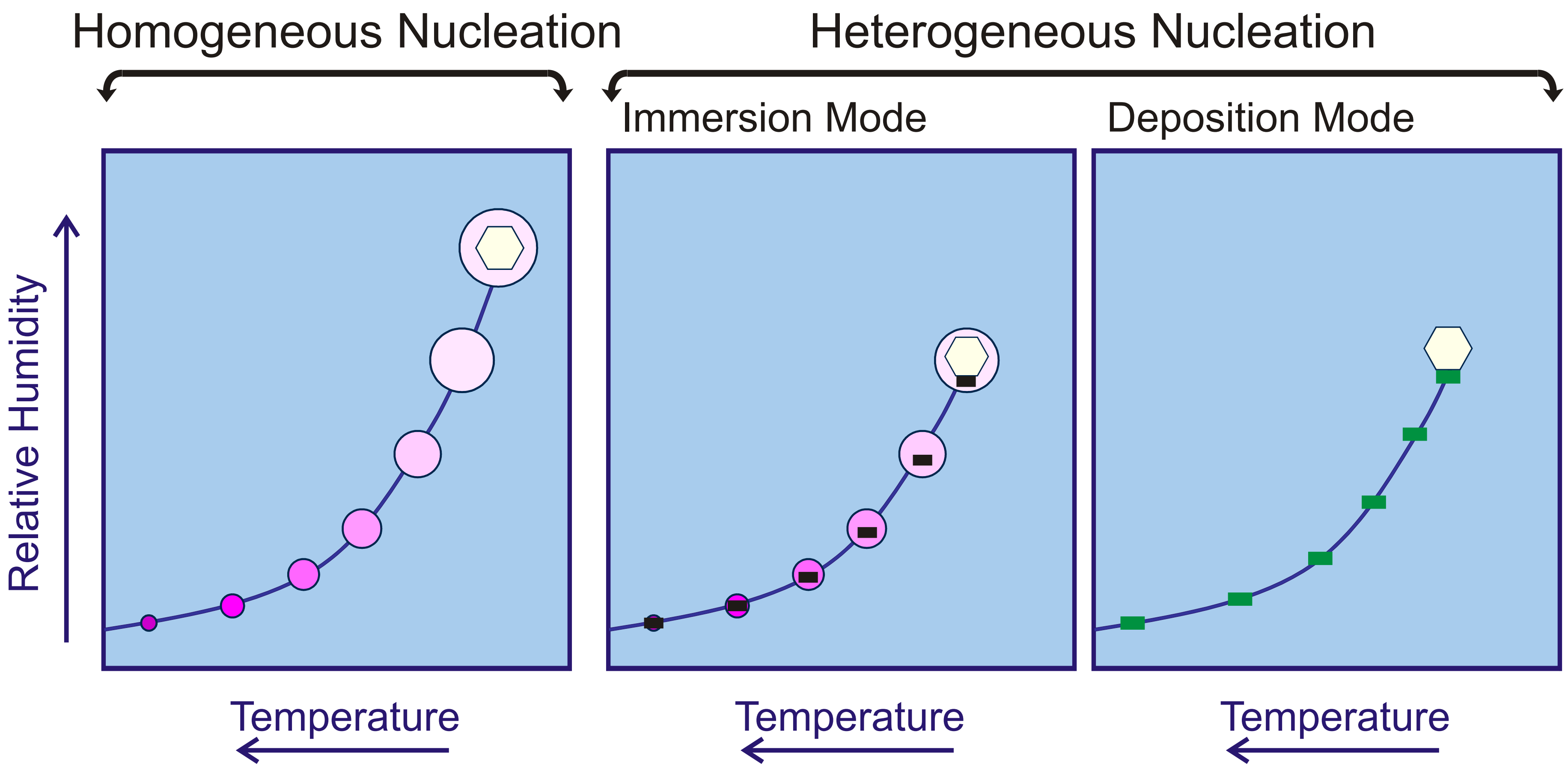
Relative Humidity
w.r.t. Ice:

$$RHI = a_{\mathrm{w}} \cdot \frac{p_{liq}}{p_{ice}}$$

Ice nucleation studies in AIDA chamber

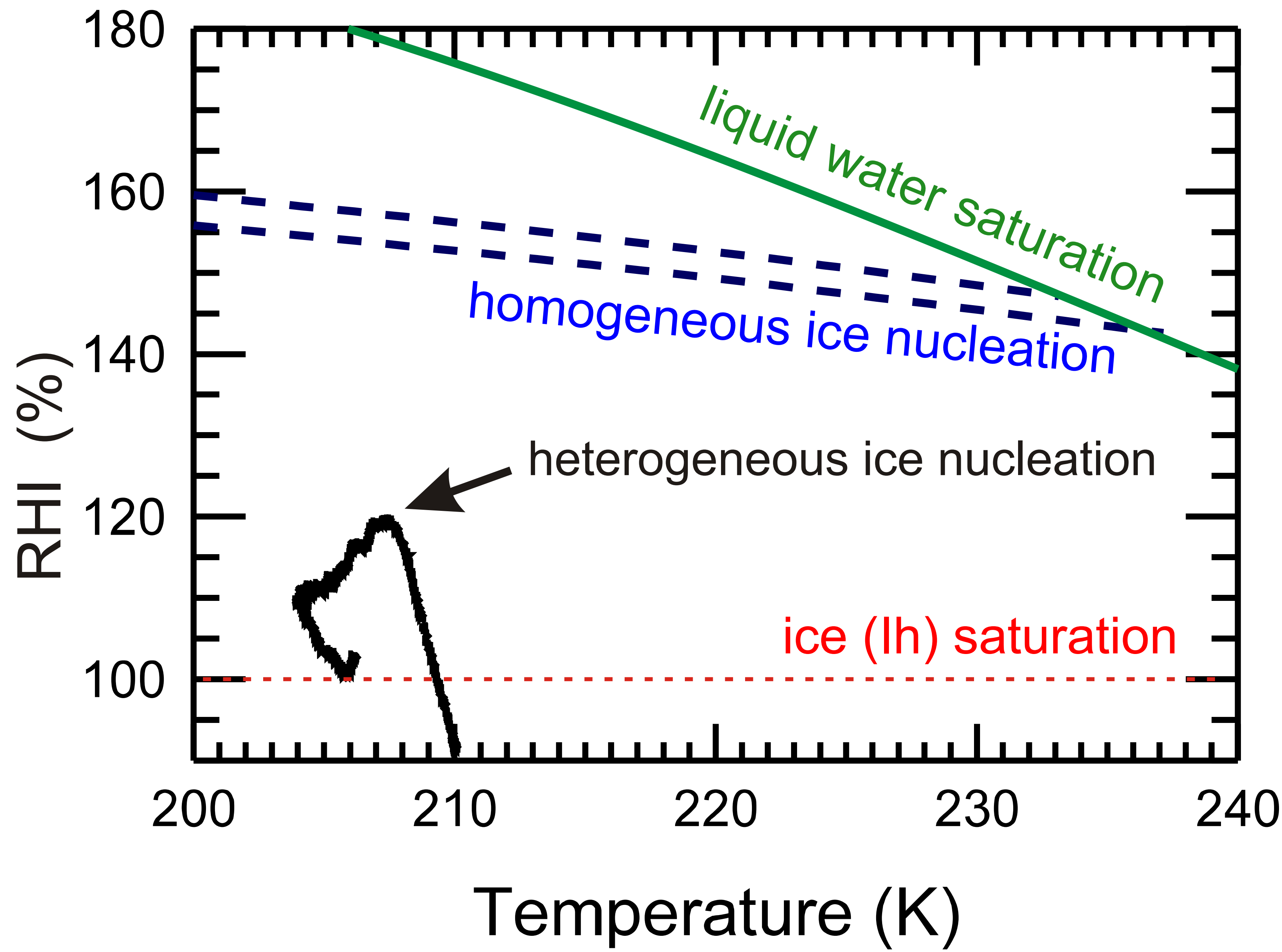
Möhler et al.



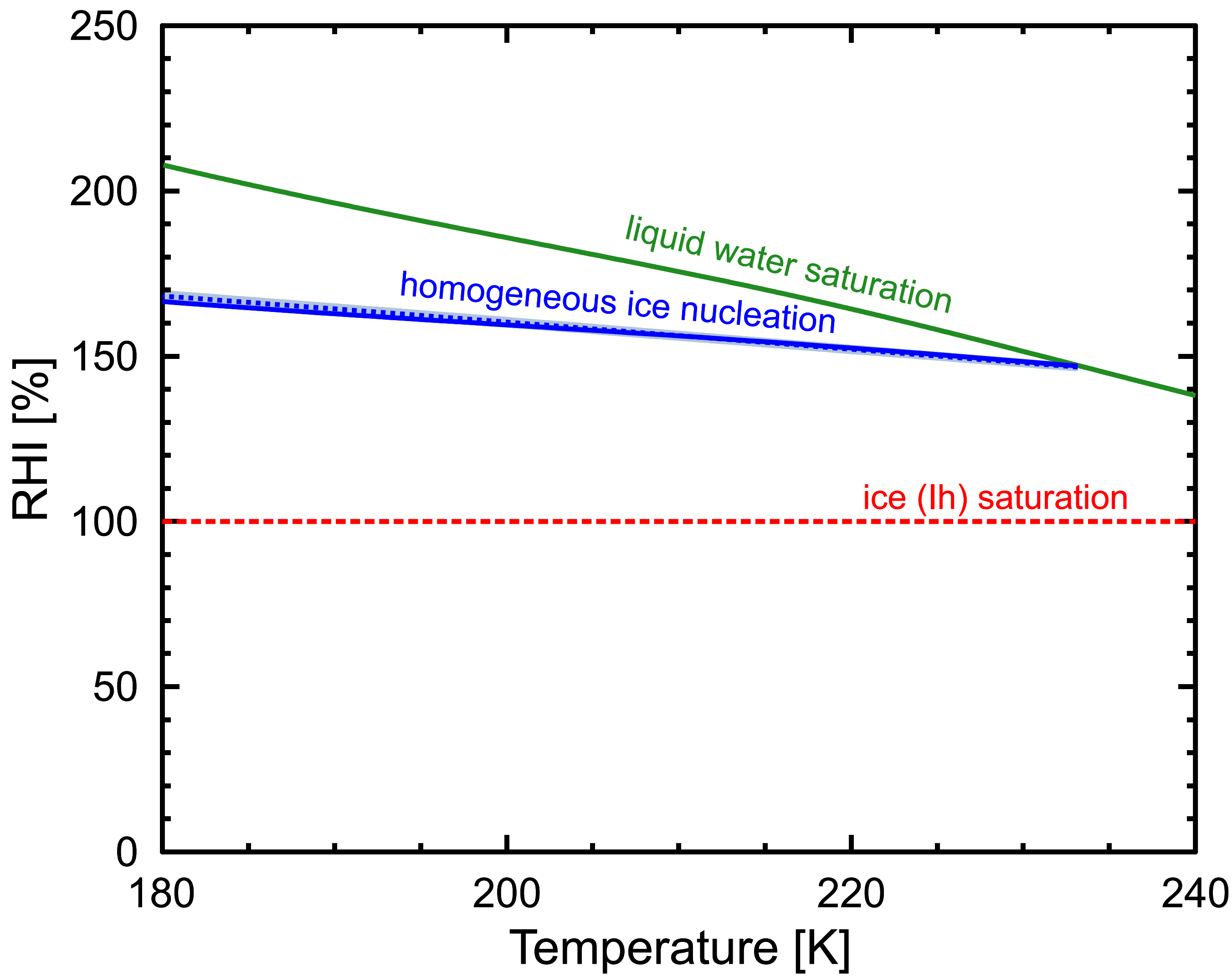

Homogeneous Nucleation
Heterogeneous Nucleation
Immersion Mode
Deposition Mode
Relative Humidity
Temperature
Temperature
Temperature

Ice nucleation studies in AIDA chamber

Möhler et al., ERL 2008

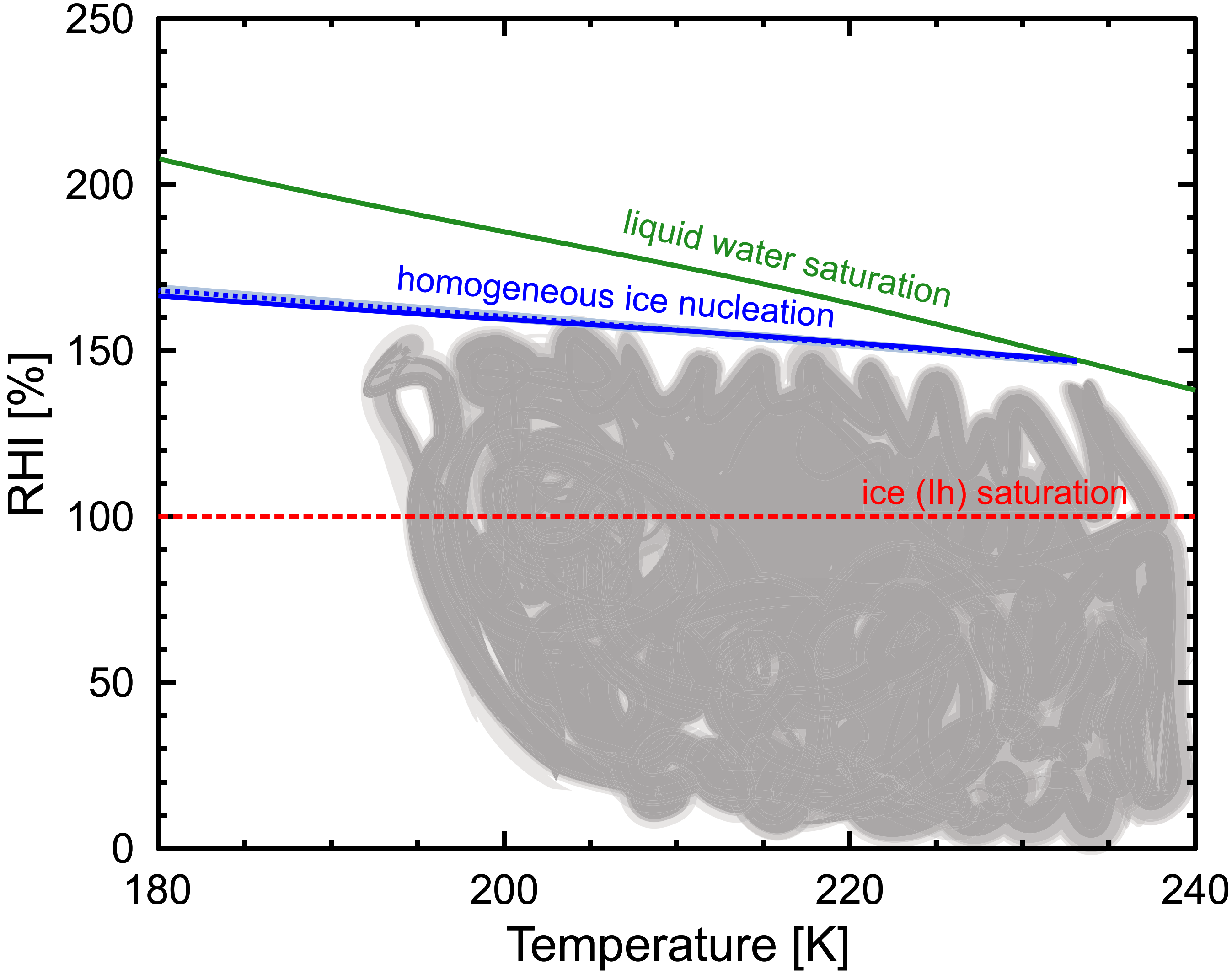


Clear air



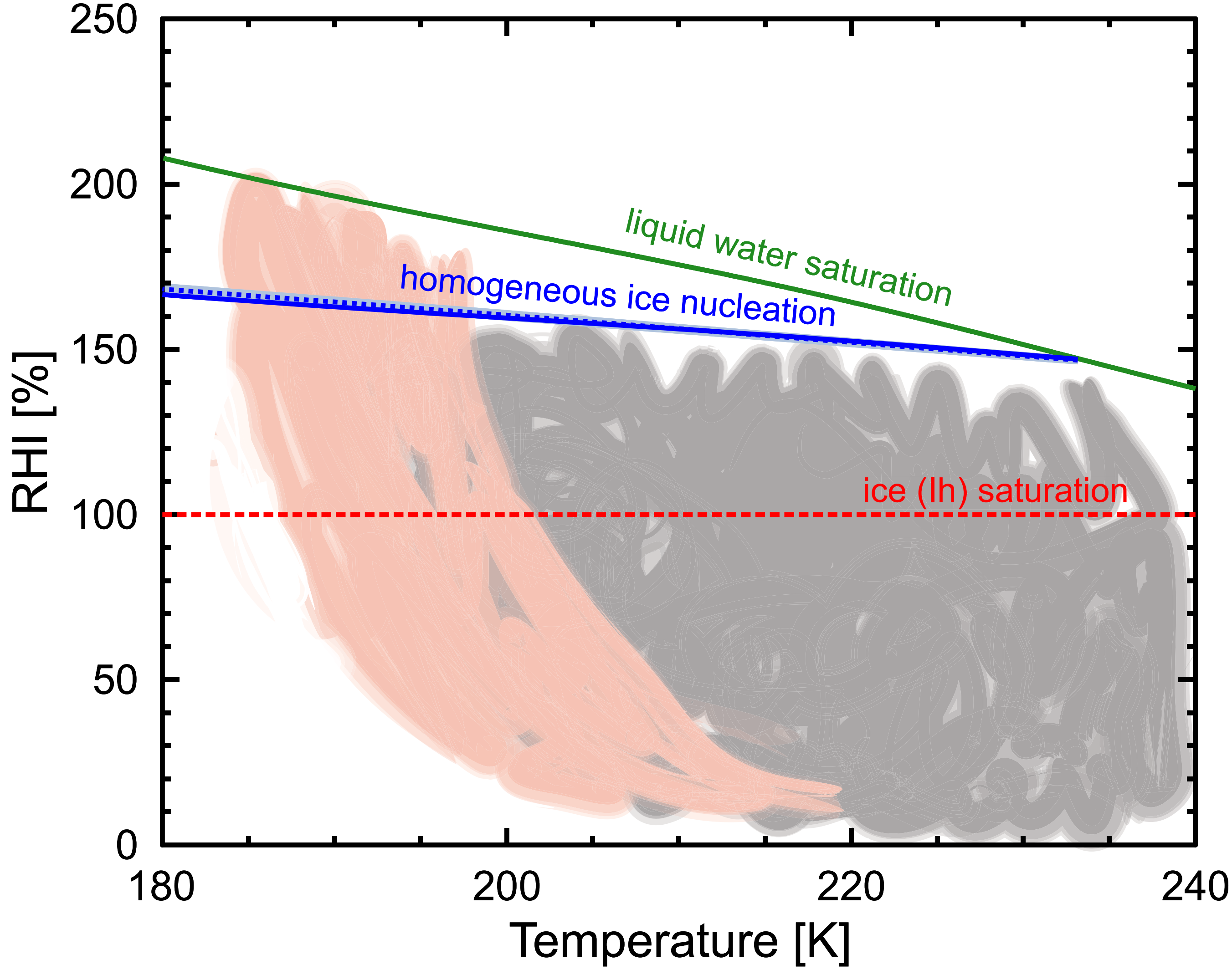
liquid water saturation
homogeneous ice nucleation
ice (Ih) saturation
RHI [%]
Temperature [K]
0
50
100
150
200
250
180
200
220
240

Clear air



250
200
150
100
50
0
RHI [%]
180
200
220
240
Temperature [K]
liquid water saturation
homogeneous ice nucleation
ice (Ih) saturation

Clear air



liquid water saturation
homogeneous ice nucleation
ice (Ih) saturation
RHI [%]
Temperature [K]
250
200
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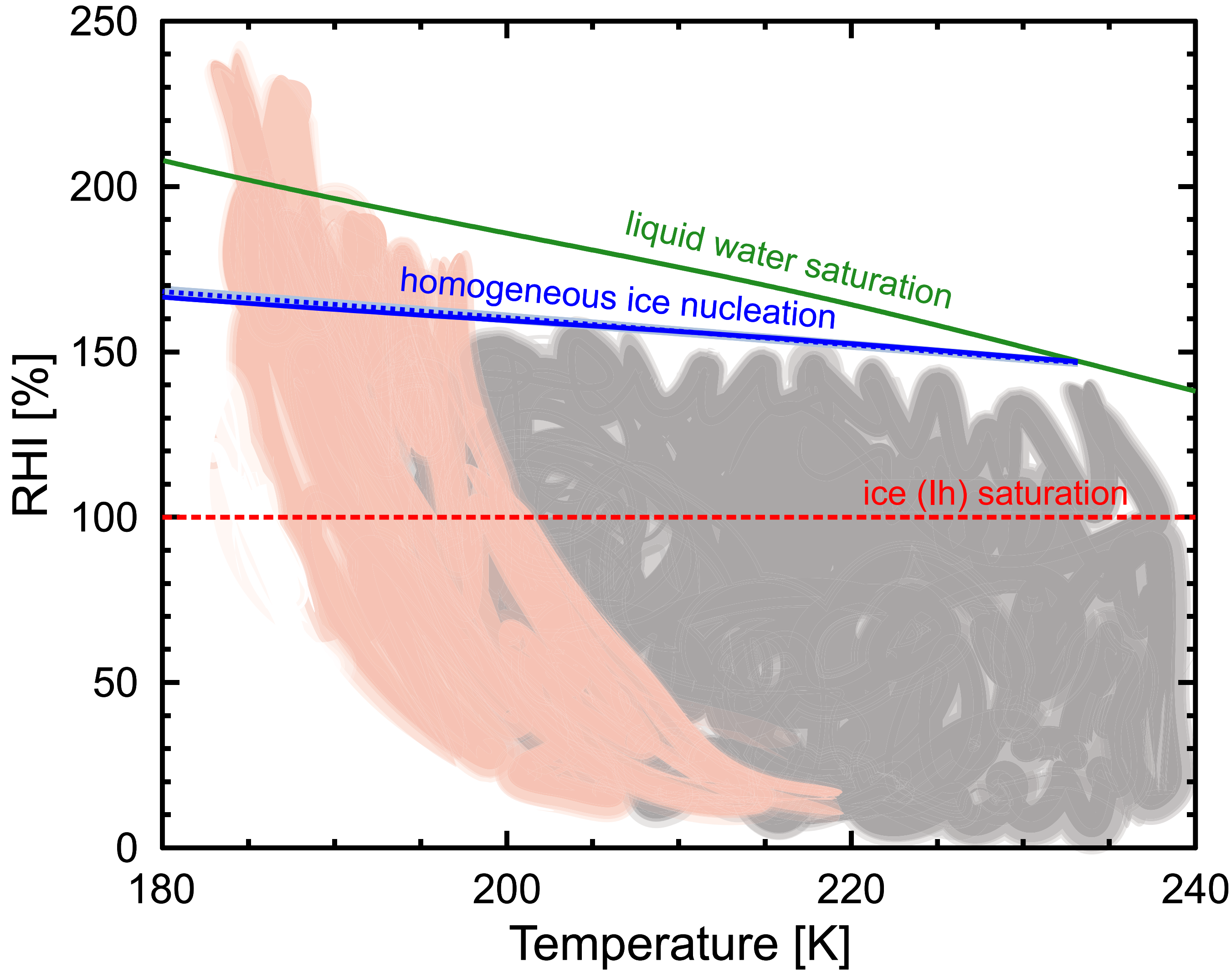
Clear air



250
200
150
100
50
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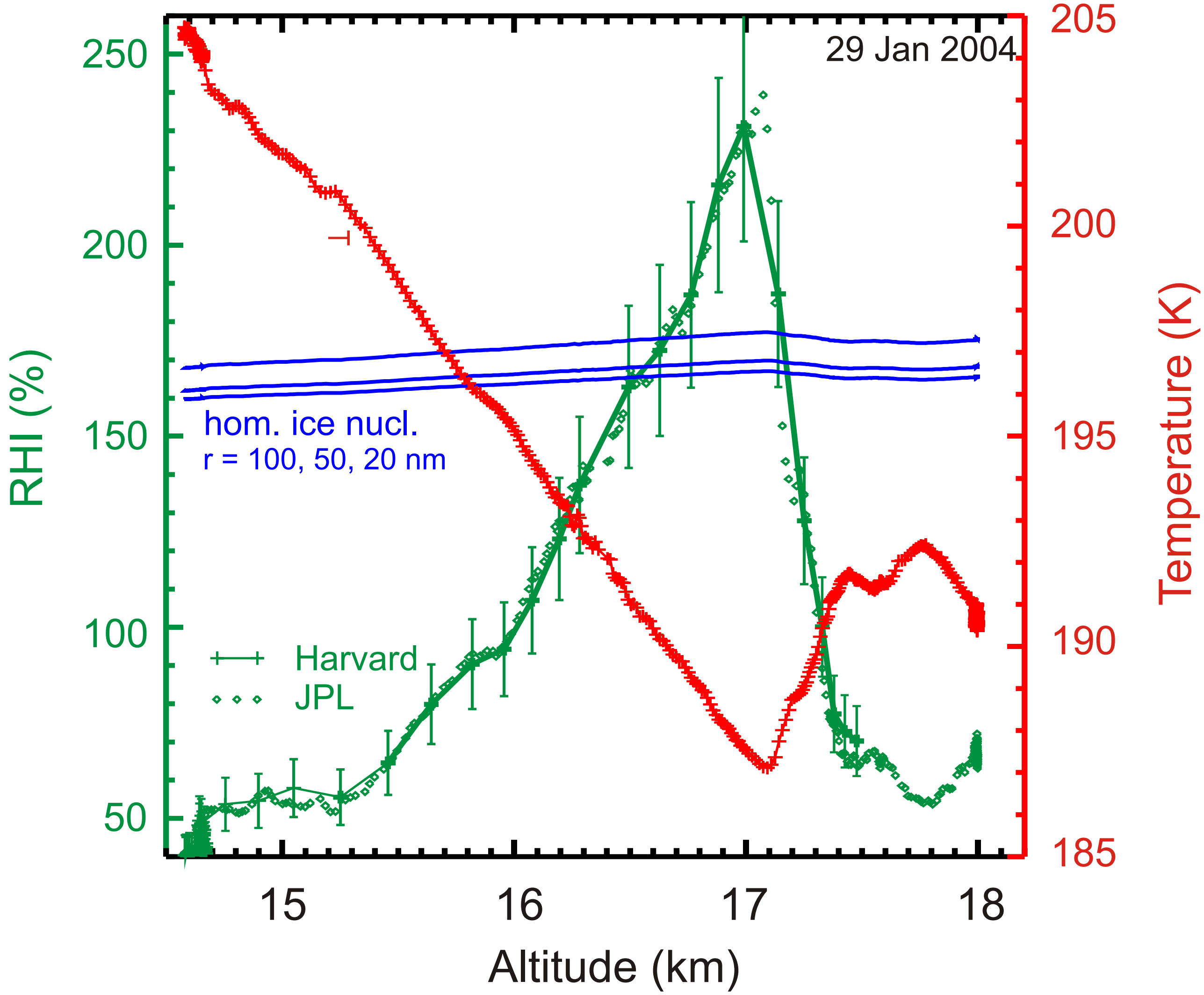
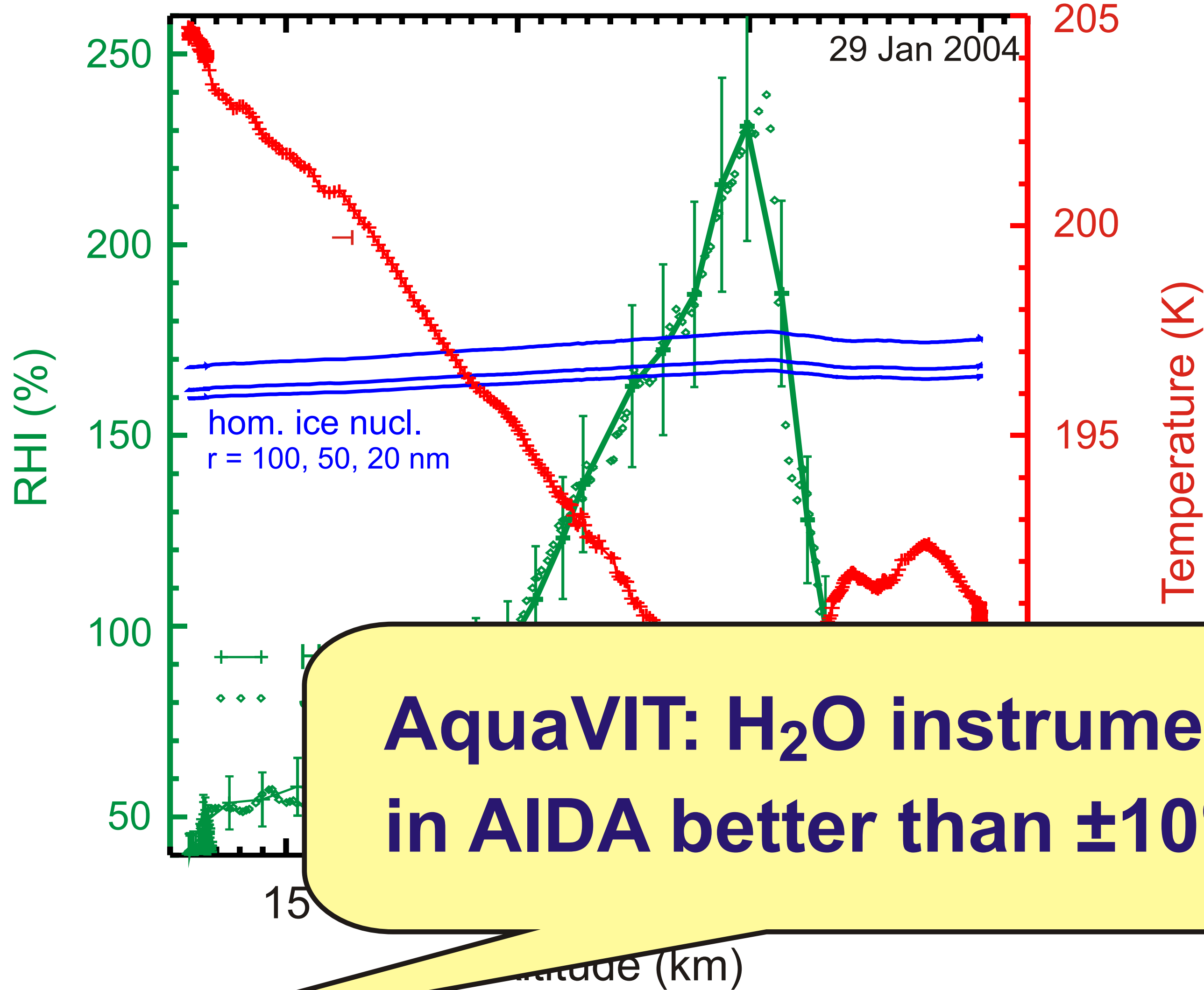
RHI [%]
Temperature [K]
liquid water saturation
homogeneous ice nucleation
ice (Ih) saturation

Clear air



Jensen et al., ACP 2005

Clear air

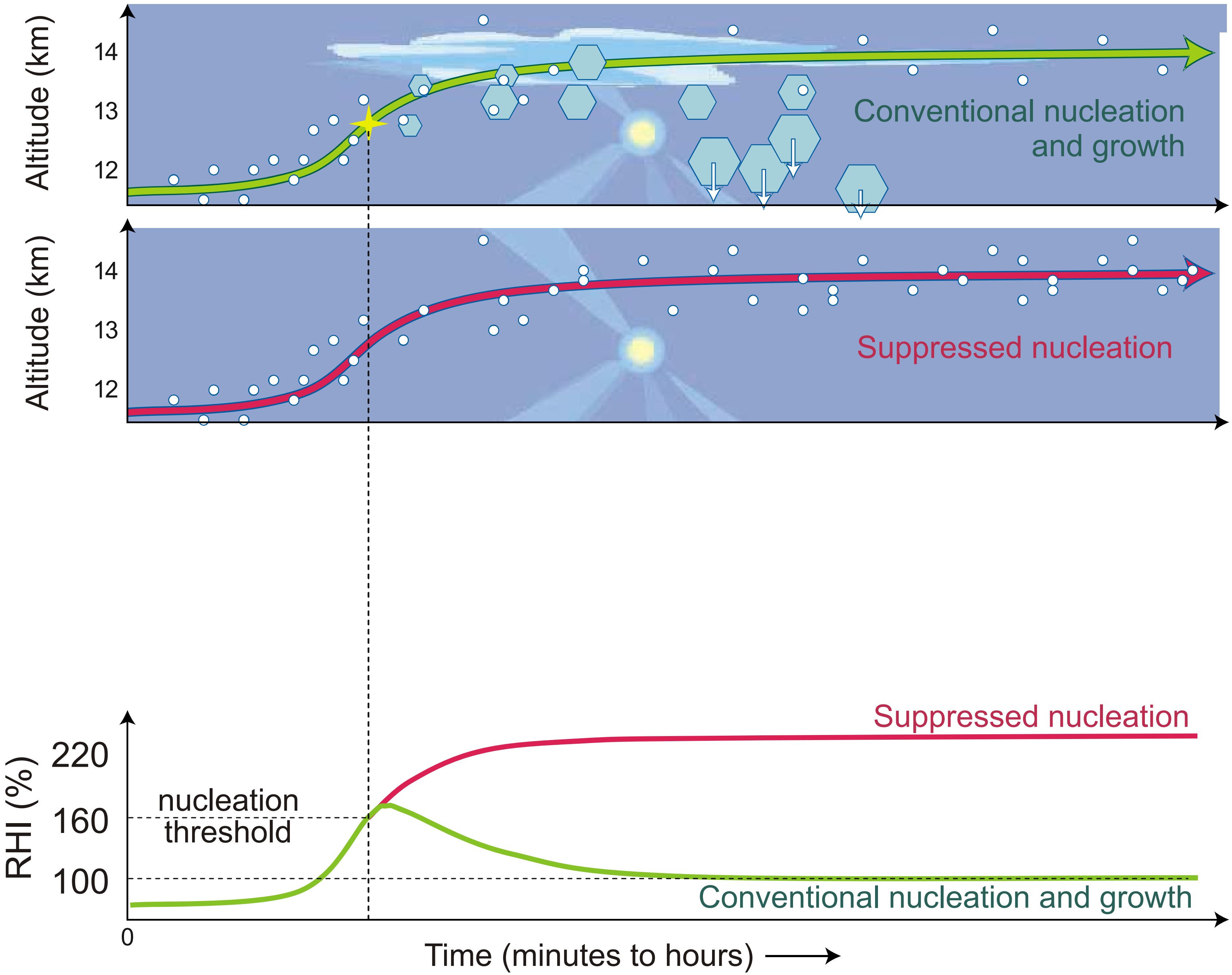


AquaVIT: H_2O instruments in AIDA better than ±10%

Ottmar Möhler

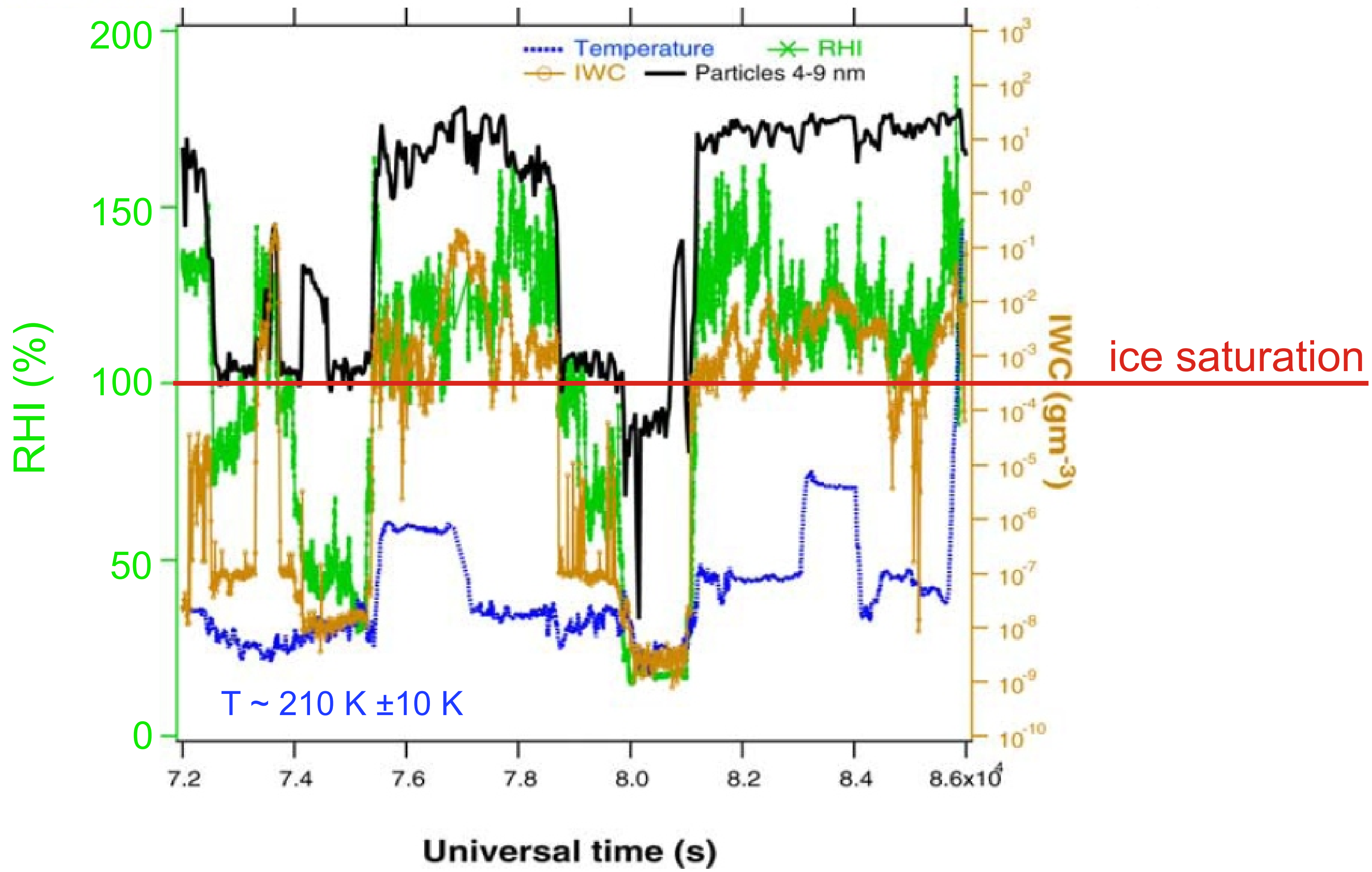
Jensen et al., ACP 2005

When dry air is too humid: the clear-air puzzle



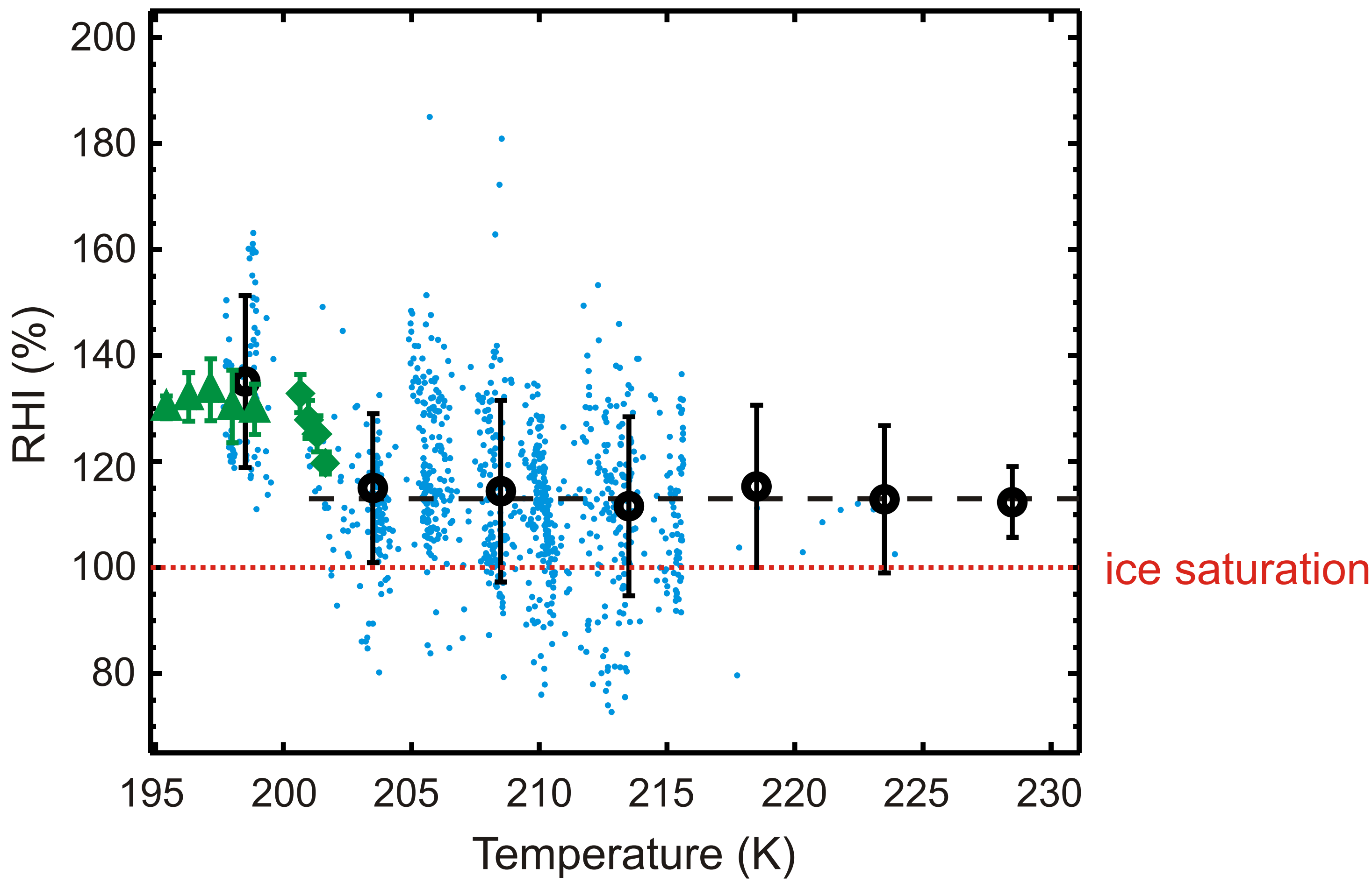
Peter, Marcolli, Spichtinger, Corti, Baker, Koop, Science 2006

Inside cirrus clouds



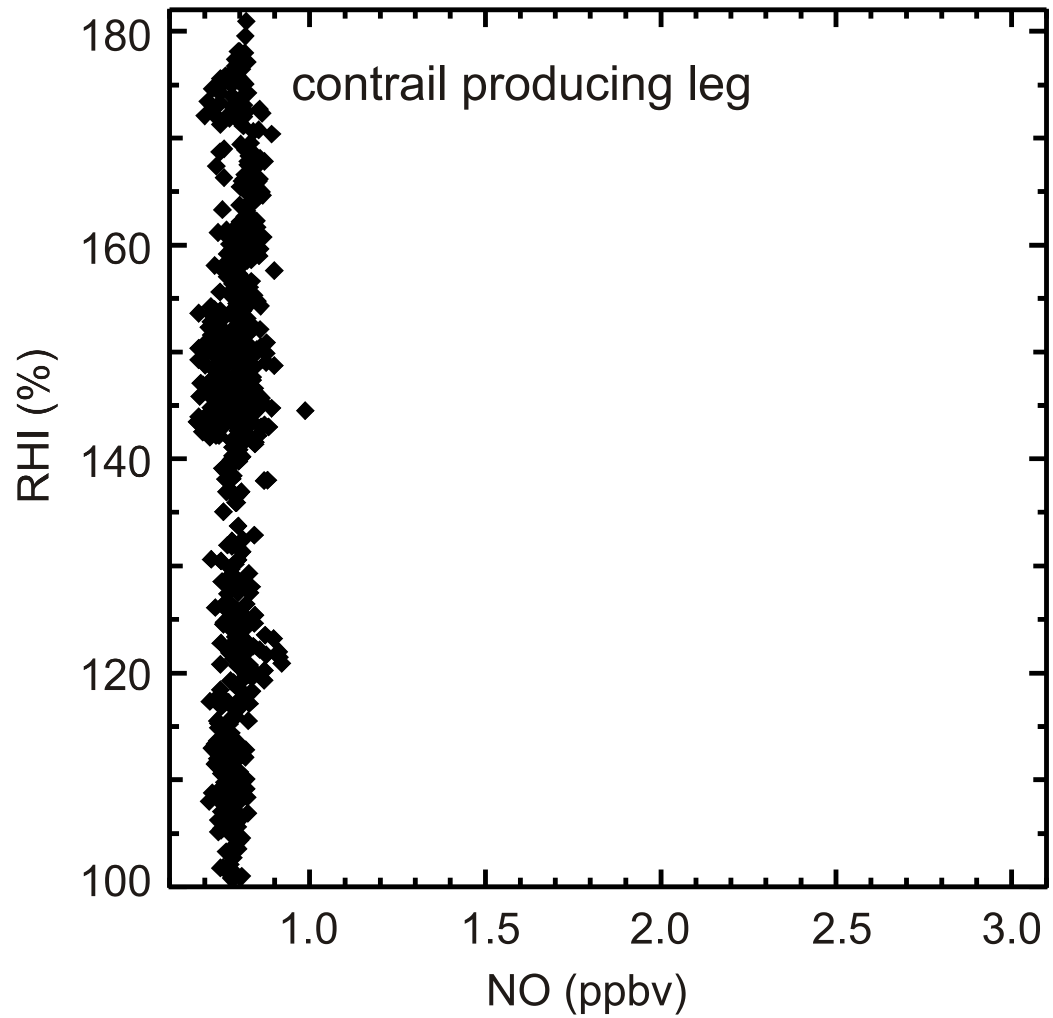
Lee et al., JGR 2004

Inside cirrus clouds



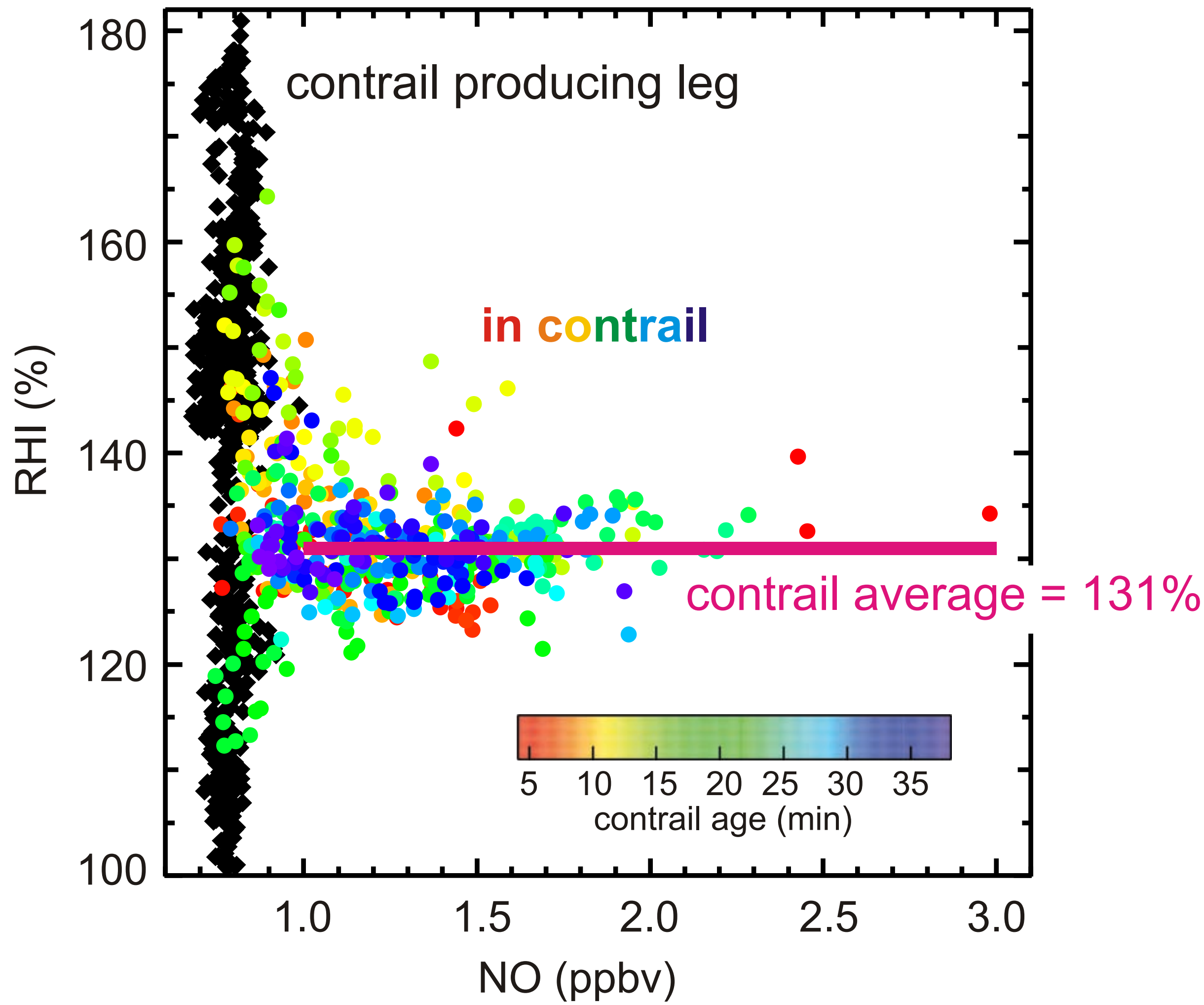
Gao et al., Science 2004

Inside contrails



Gao et al., Atmos. Env. 2006

Inside contrails



Gao et al., Atmos. Env. 2006

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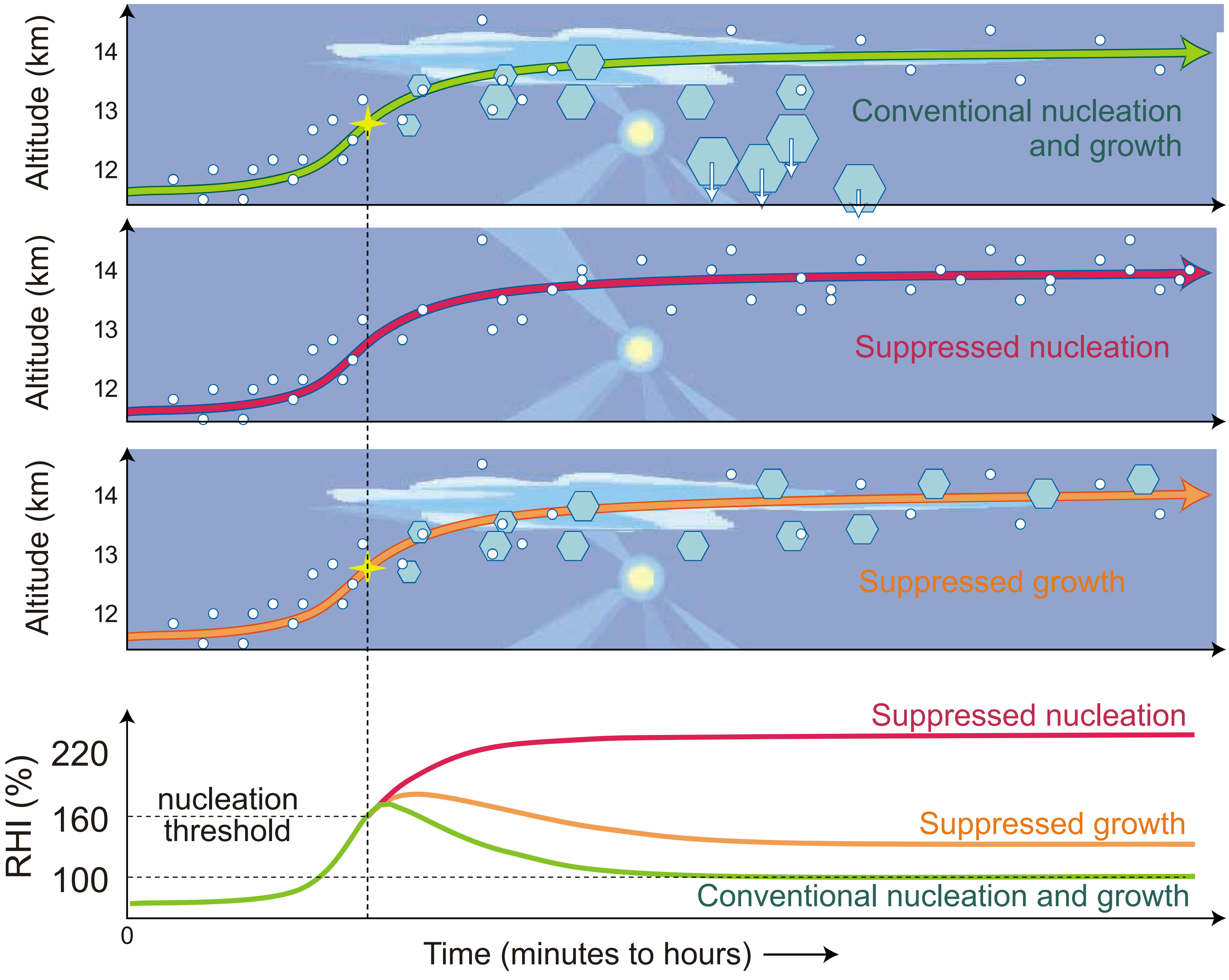
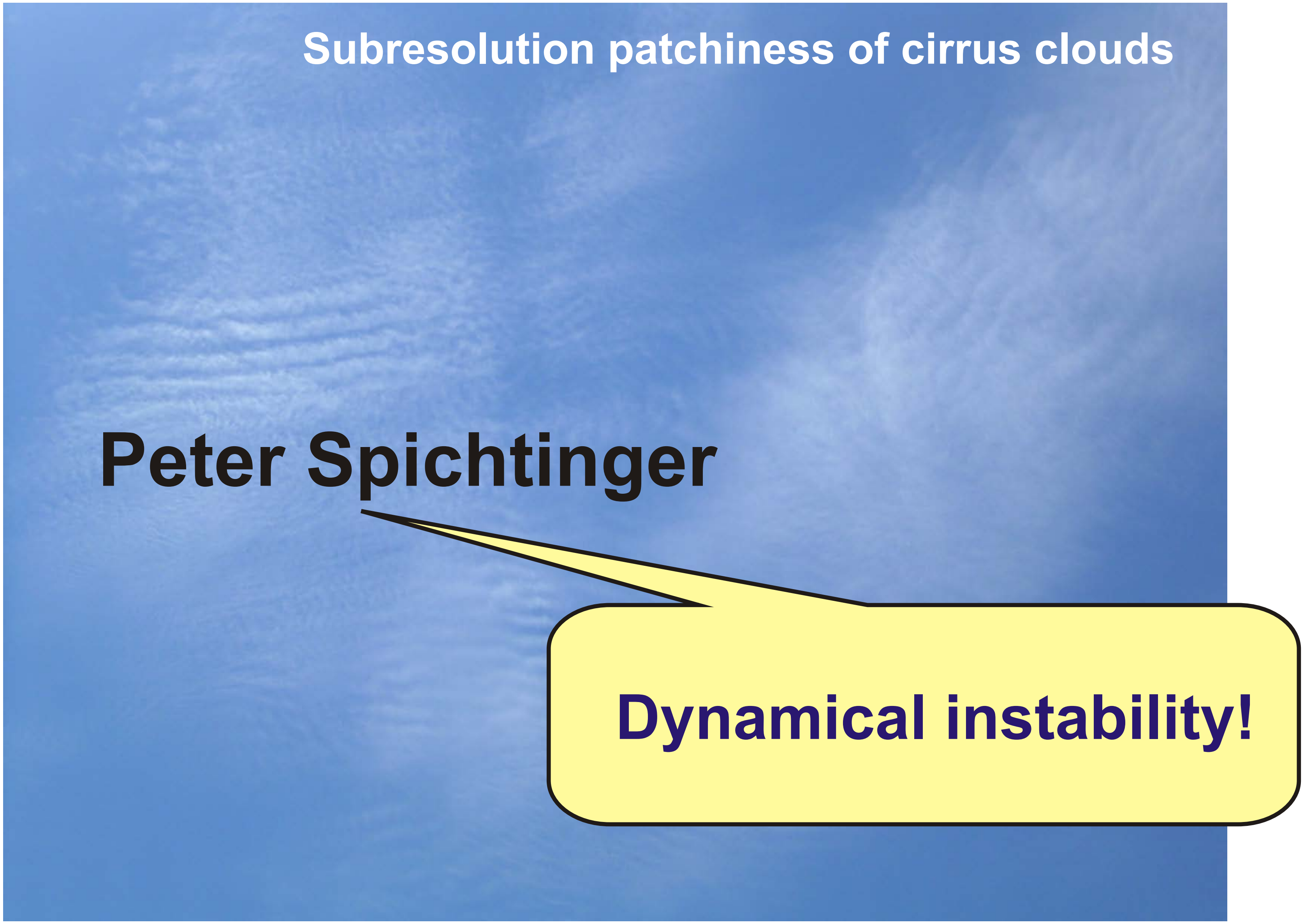


Peter, Marcolli, Spichtinger, Corti, Baker, Koop, Science 2006

Potential solutions to the inside-cloud puzzle

Average implies supersaturation within clouds

Potential solutions to the inside-cloud puzzle



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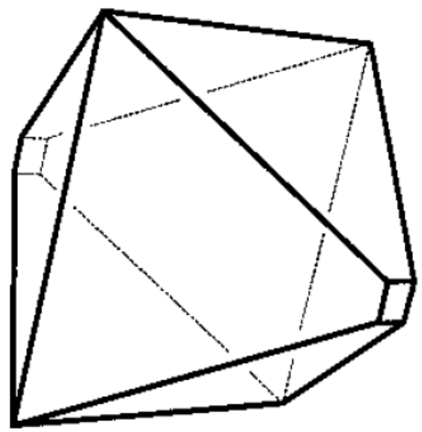
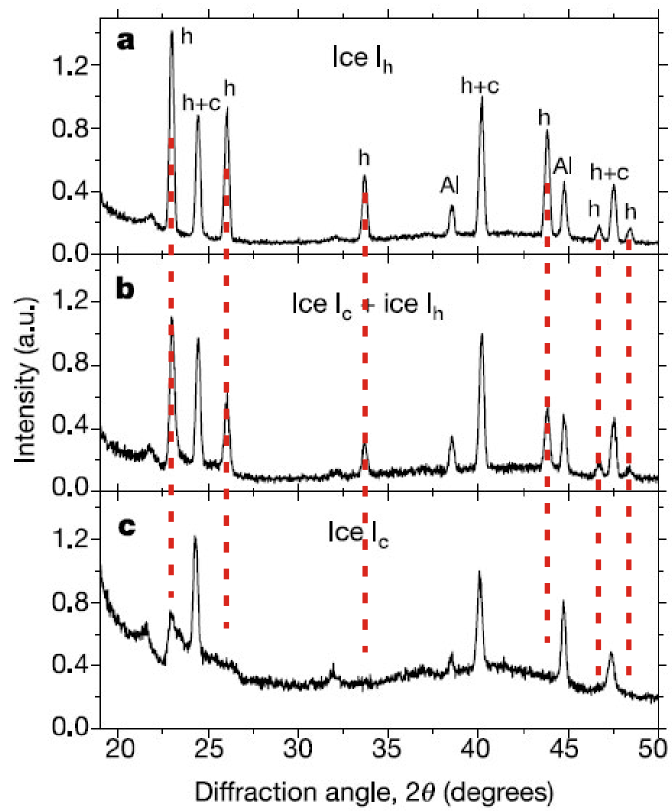
Potential solutions to the inside-cloud puzzle



Formation of cubic ice Ic



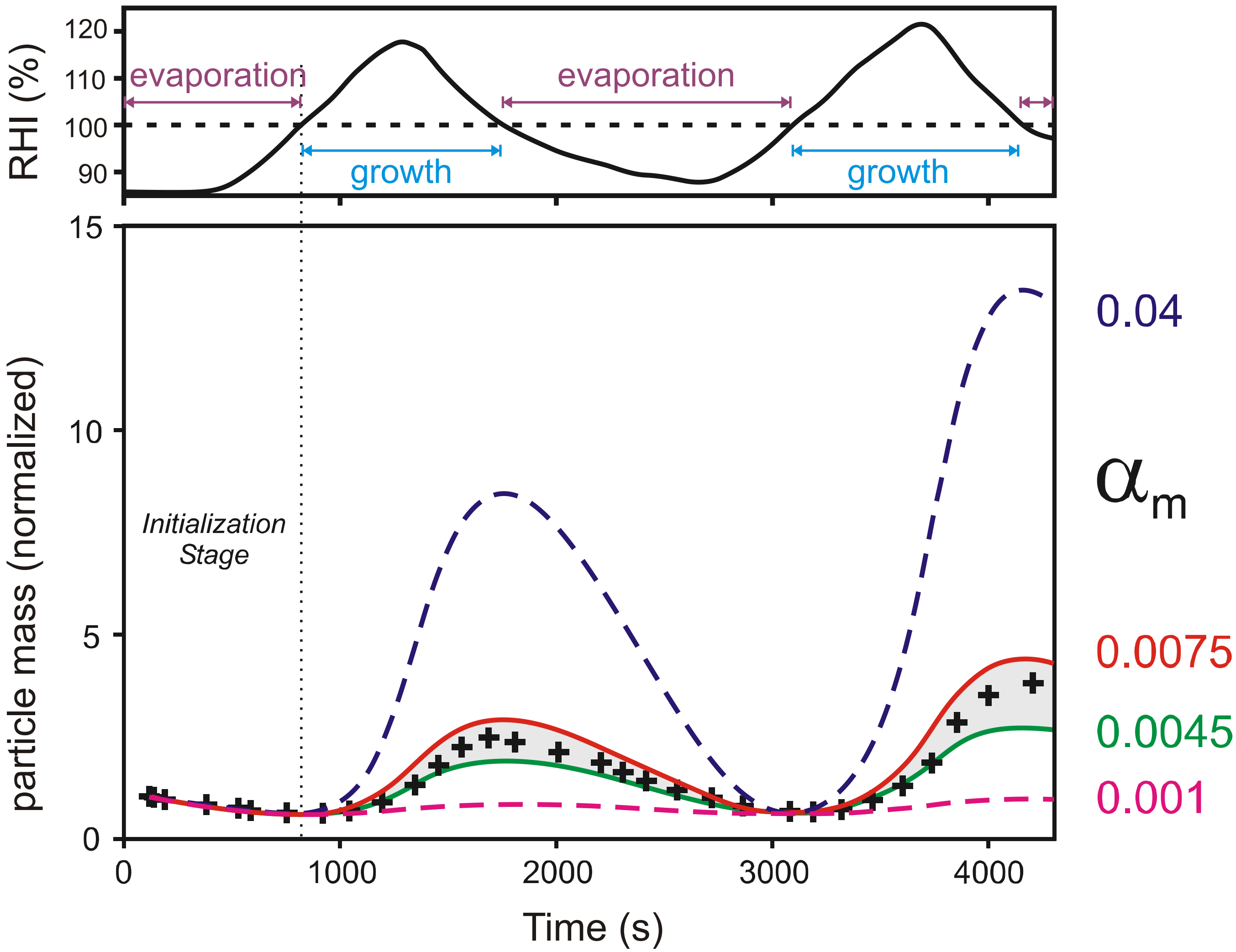
Differences in X-ray diffraction patterns

Vapor pressure of cubis ice Ic is ~10% larger than hexagonal ice Ih

Murray et al, Nature 2005
Shilling et et., GRL 2006

Potential solutions to the inside-cloud puzzle

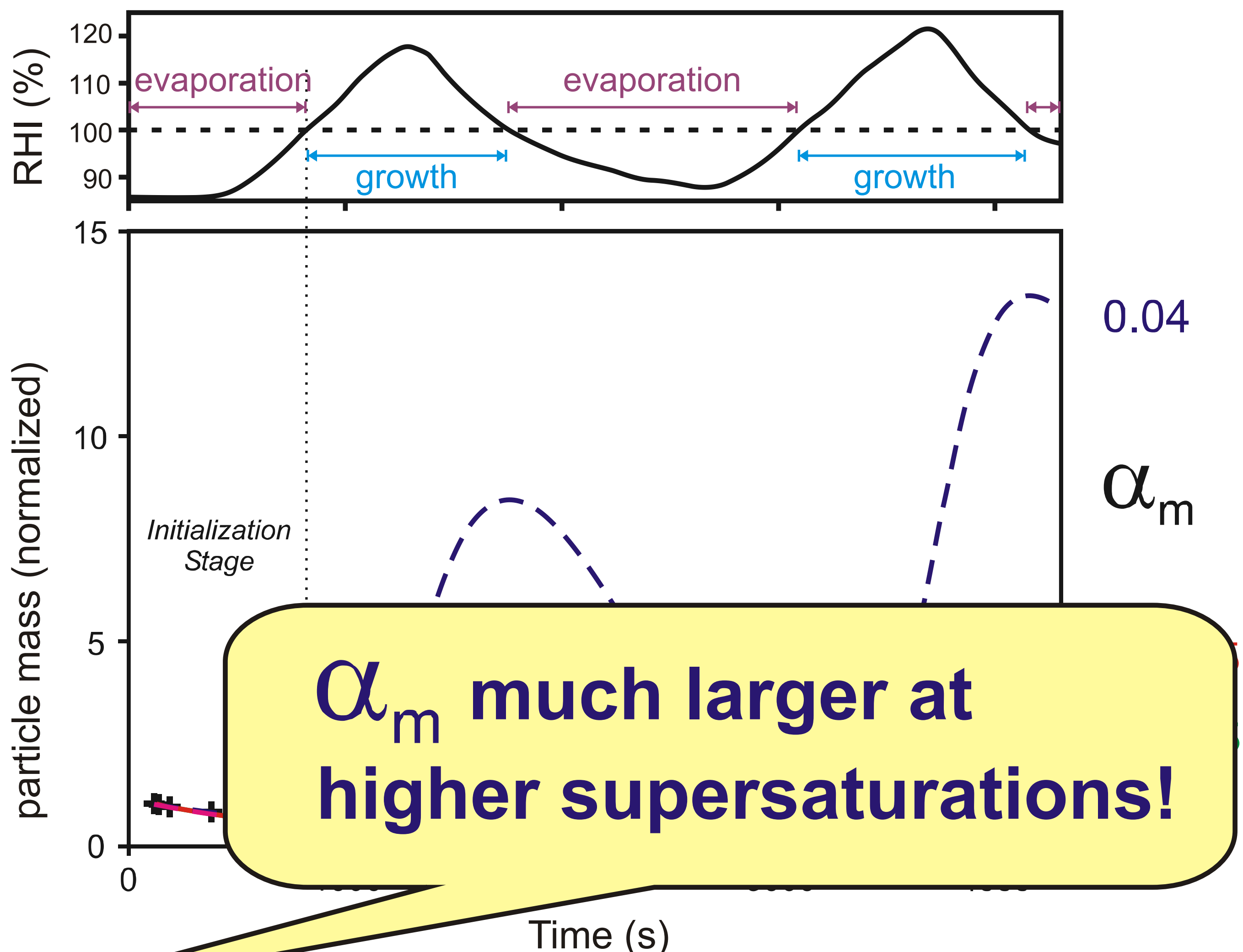
Mass accommodation coefficient of water on ice



Magee et al., GRL 2006

Potential solutions to the inside-cloud puzzle

Mass accommodation coefficient of water on ice



α_m much larger at higher supersaturations!

Tom Peter

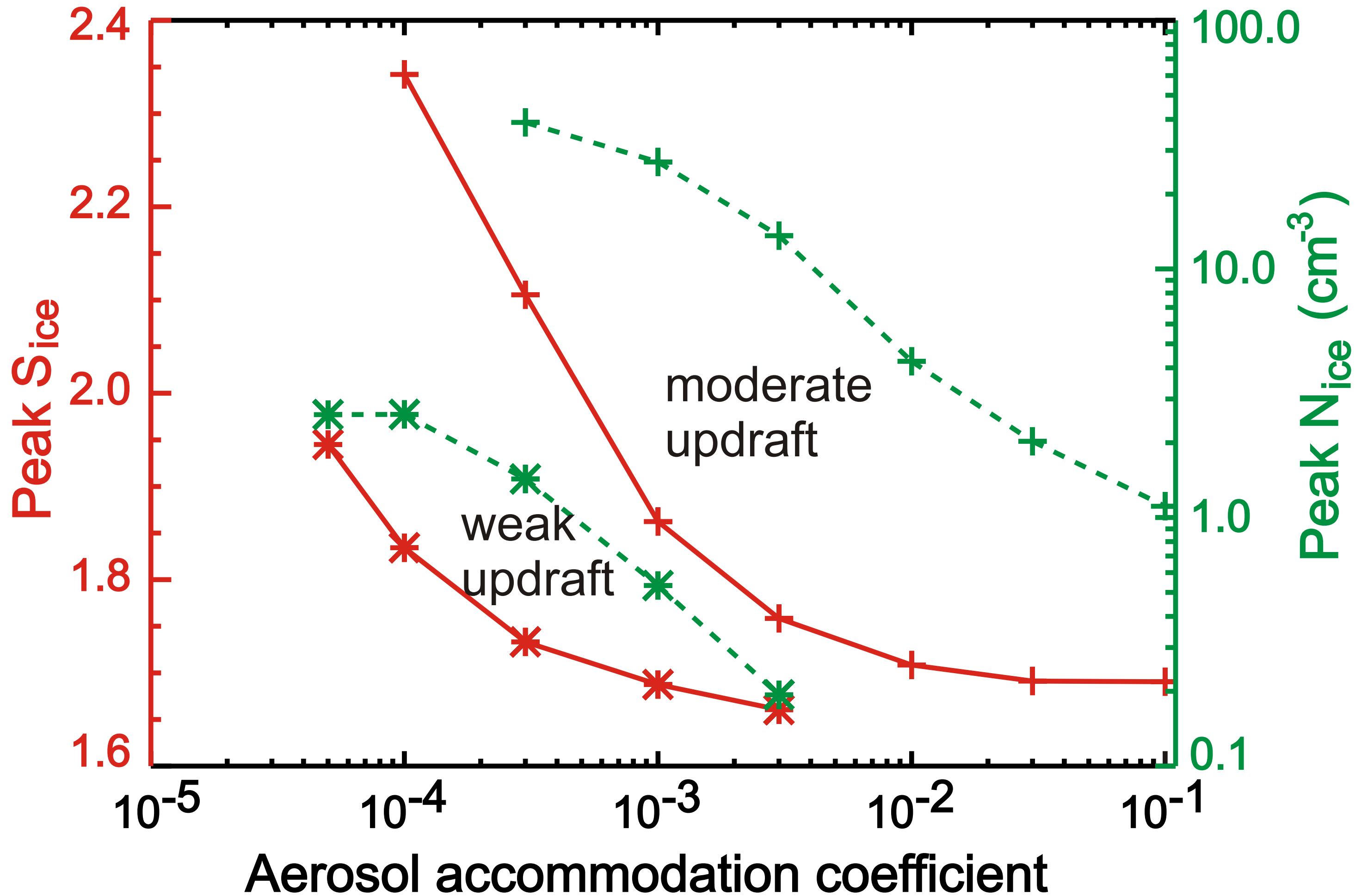
Magee et al., GRL 2006

Potential solutions to the inside-cloud puzzle

• Measurement uncertainties?	no, probably not large enough
• HNO_3?	no evidence from lab or thermodynamics
• Cubic ice?	yes, but only ~10% effect
• Small α_m of water on ice crystals?	probably yes, but only at low supersaturations
• Small scale patchiness?	yes

Potential solutions to the clear-air puzzle

- Lack of preexisting aerosol particles   no evidence
- Small α_m also on aerosols?

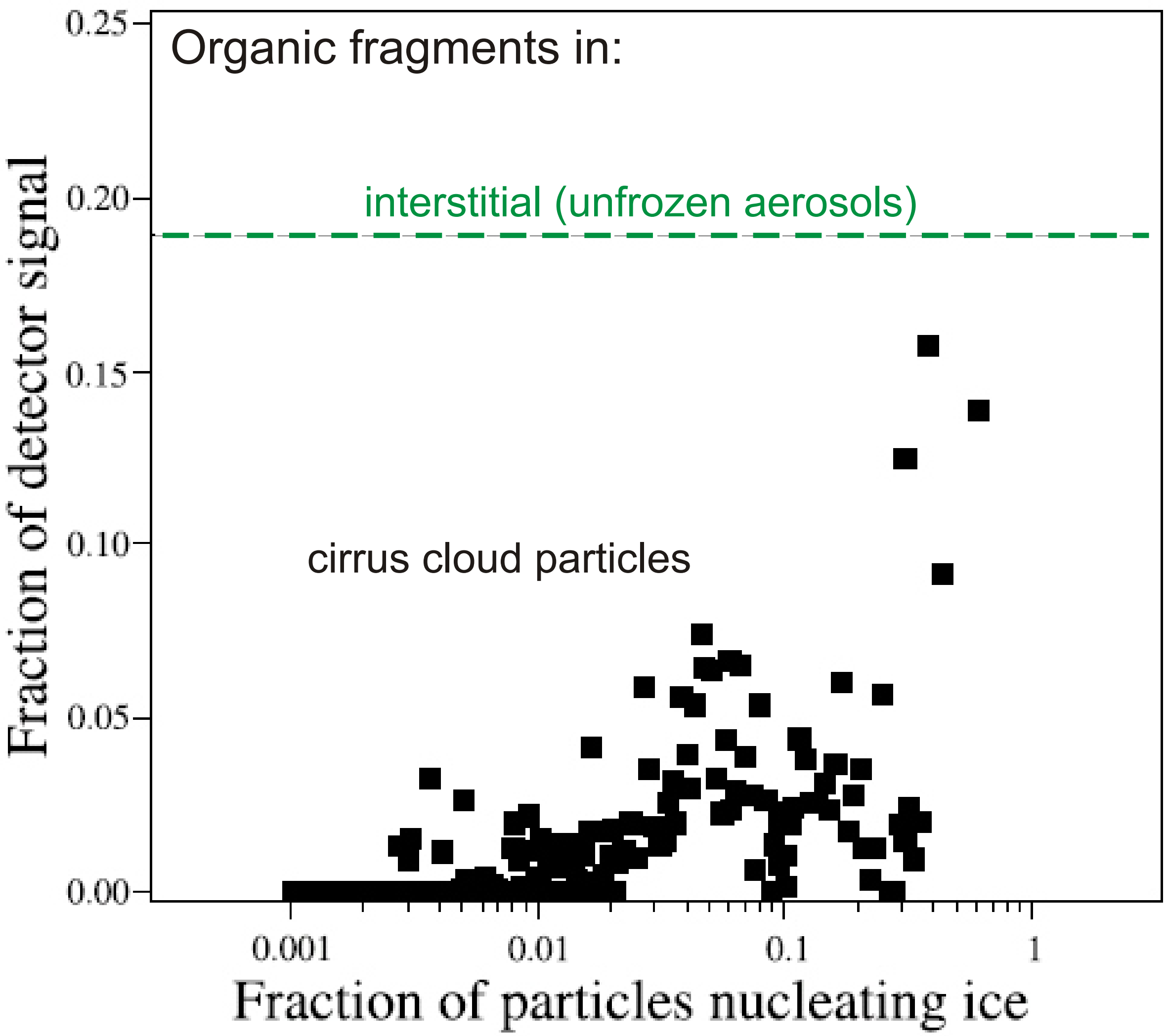


Jensen et al., ACP 2005

Dan Murphy

Upper tropospheric aerosols contain 60-80% organics!

Organics and Ice Nucleation

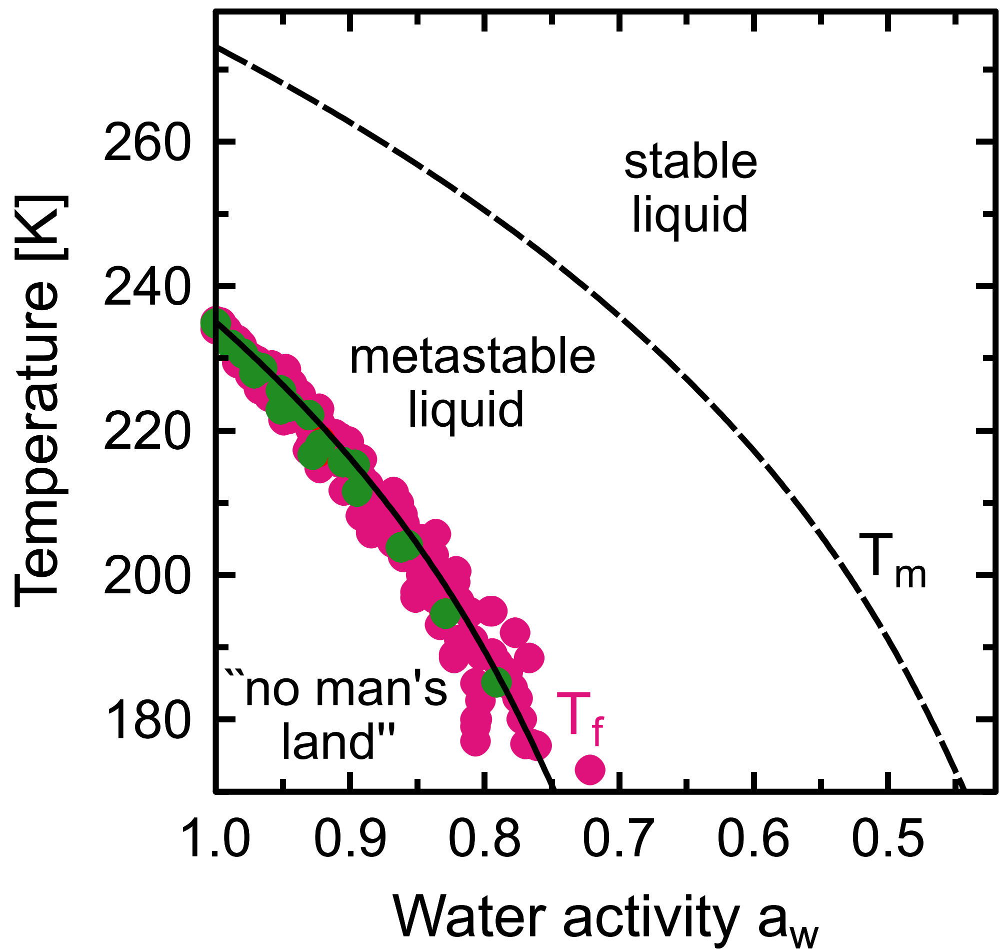


Cziczo et al., GRL, 2004

CRYSTAL-FACE
11-15 km, 196-225 K

⇒ organic aerosols are inefficient ice nucleators

Homogeneous Ice Nucleation in Aqueous Solution Droplets



inorganic solutes

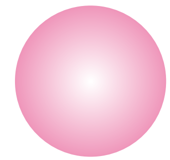
organic solutes (ethylene glycol, glycerol, glucose, urea)

⇒ nucleation rate coefficient parameterization also works for organics

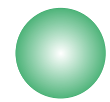
Solute mass fraction in aerosol droplets at 80% RH:

inorganic solutes:	
NaCl	0.23
H_2SO_4	0.27
$(NH_4)_2SO_4$	0.43
organics:	
oxalic acid	0.50
glycerol	0.51
succinic acid	0.61
glucose	0.65
octanetetrol	0.69
levoglucosan	0.70
sucrose	0.70
HMMA	0.80

more water
→ larger



less water
→ smaller



=> organic aerosol particles exhibit larger solute mass fractions

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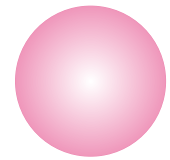

organics:

oxalic acid	0.50
glycerol	0.51
succinic acid	0.61
glucose	0.65
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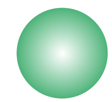
levoglucosan	0.70
sucrose	0.70
HMMA	0.80

less water
→ smaller



=> organic aerosol particles exhibit larger solute mass fractions

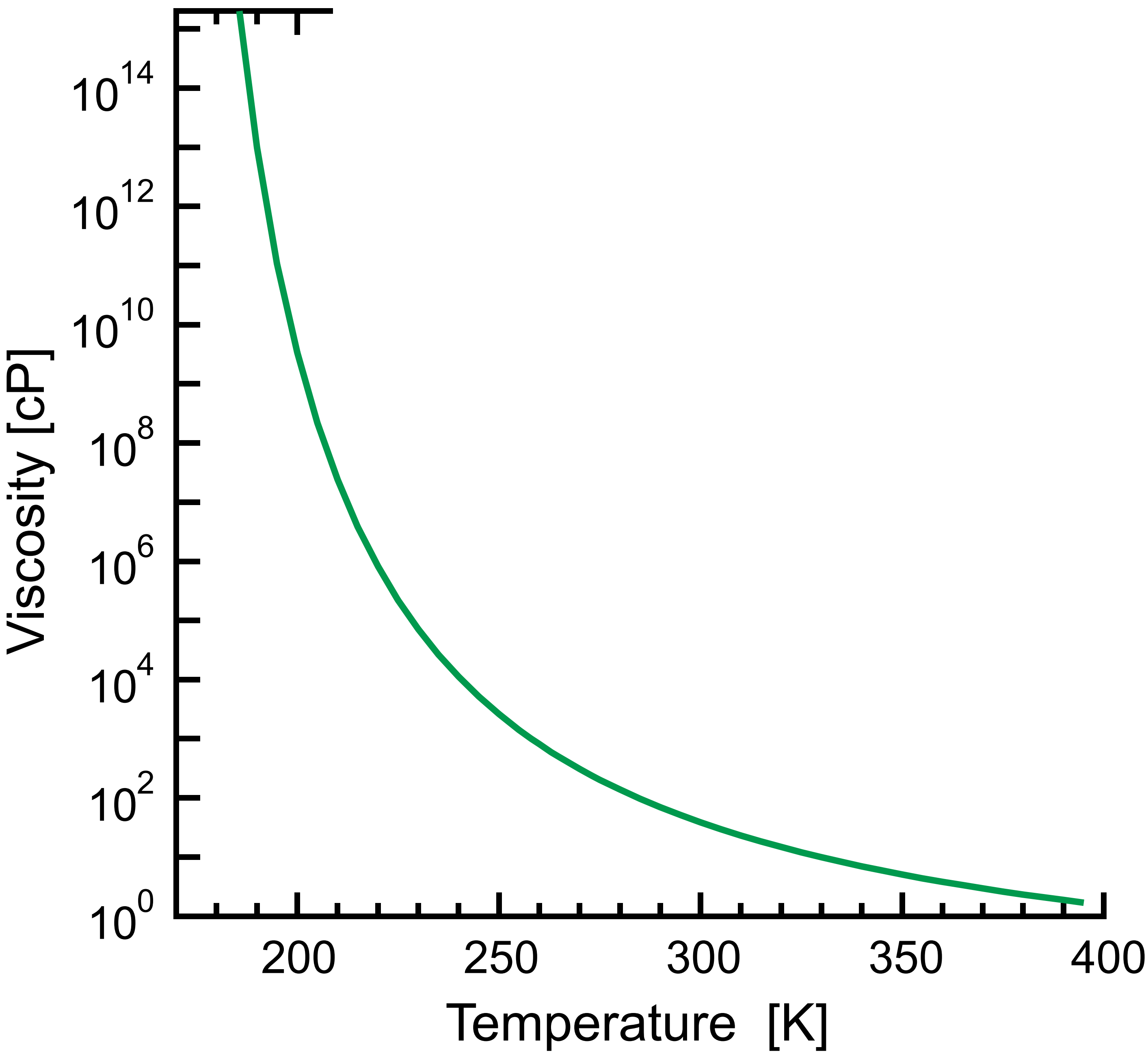
Marcolli et al., J.Phys.Chem.A, 2004:

In multi-component organic aerosol particles, solutes are less likely to preciptate

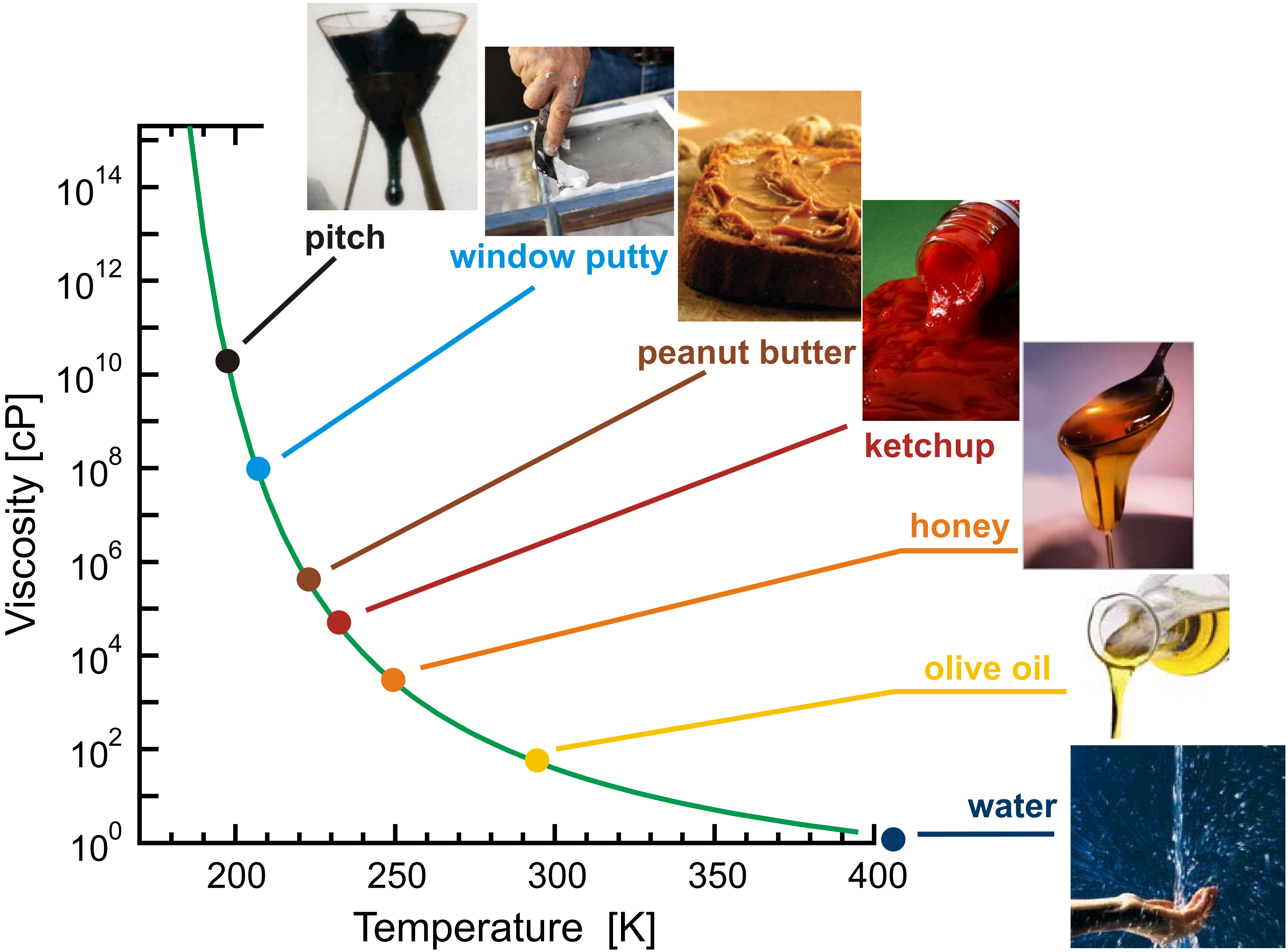
=> likely in a liquid state

Liquids can show quite different mechanical properties

e.g. viscosity / fluidity



Viscosity [cP]
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
10^{4}
10^{2}
10^{0}
200
250
300
350
400
Temperature [K]



pitch
window putty
peanut butter
ketchup
honey
olive oil
water
Viscosity [cP]
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
10^{4}
10^{2}
10^{0}
200
250
300
350
400
Temperature [K]

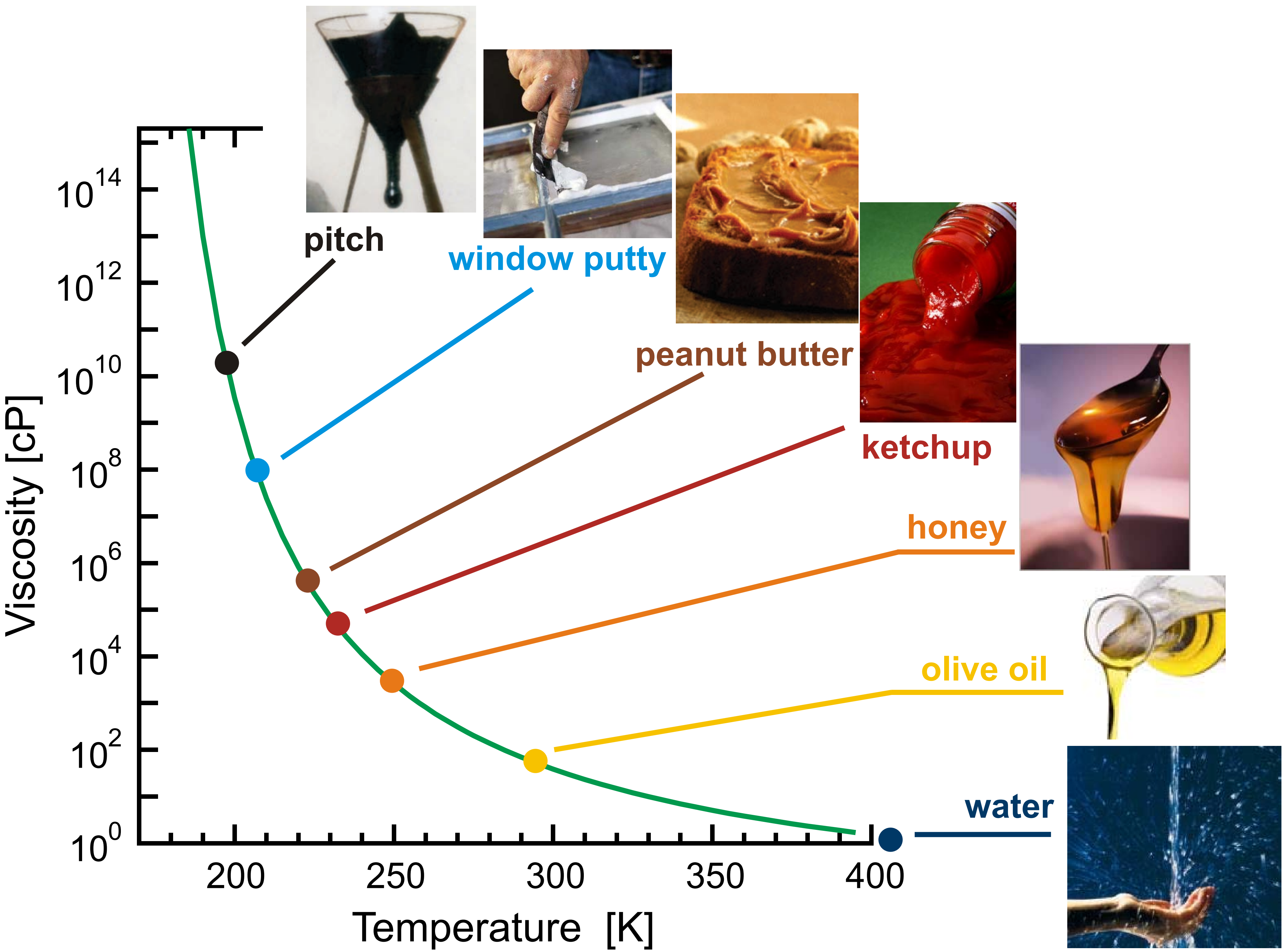
The pitch drop experiment

started by Thomas Parnell in 1927
at the University Of Queensland in Brisbane, Australia

Current custodian: John Mainstone
Photo taken 1990

Experiment Timeline

Date	Event
1927	Experiment set up
1930	The stem was cut
December 1938	1st drop fell
February 1947	2nd drop fell
April 1954	3rd drop fell
May 1962	4th drop fell
August 1970	5th drop fell
April 1979	6th drop fell
July 1988	7th drop fell
November 28, 2000	8th drop fell



pitch
window putty
peanut butter
ketchup
honey
olive oil
water
Viscosity [cP]
10^{14}
10^{12}
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300
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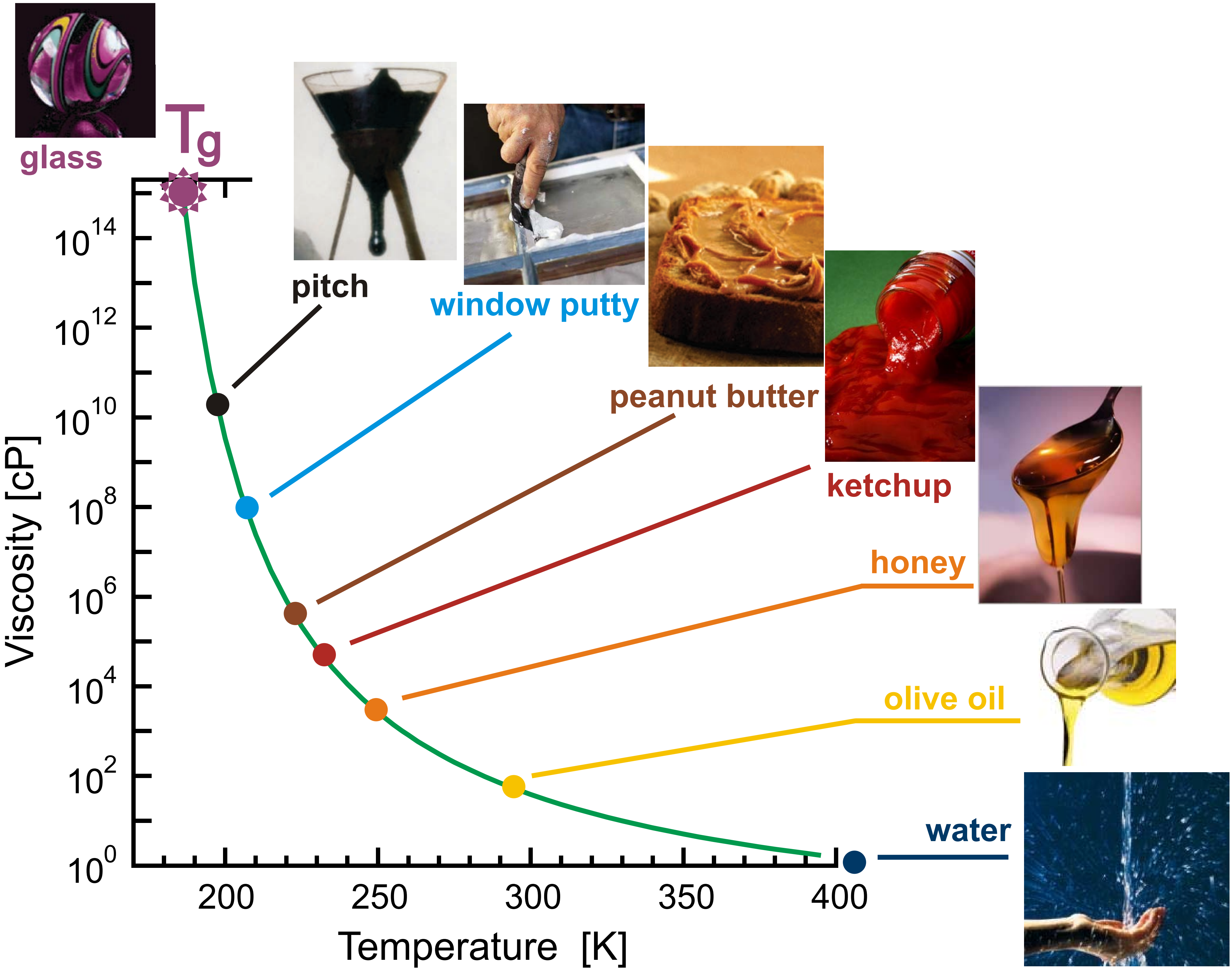
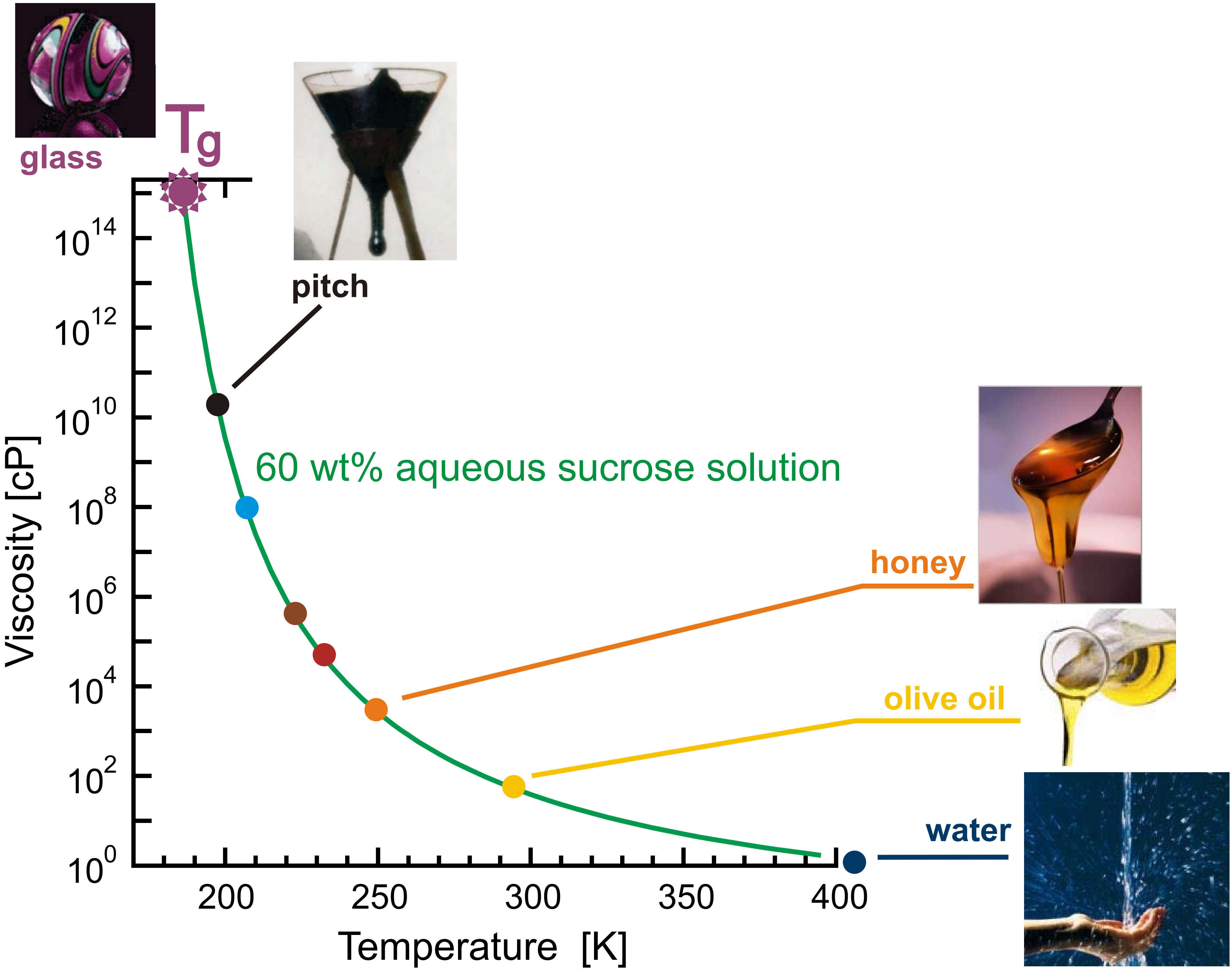
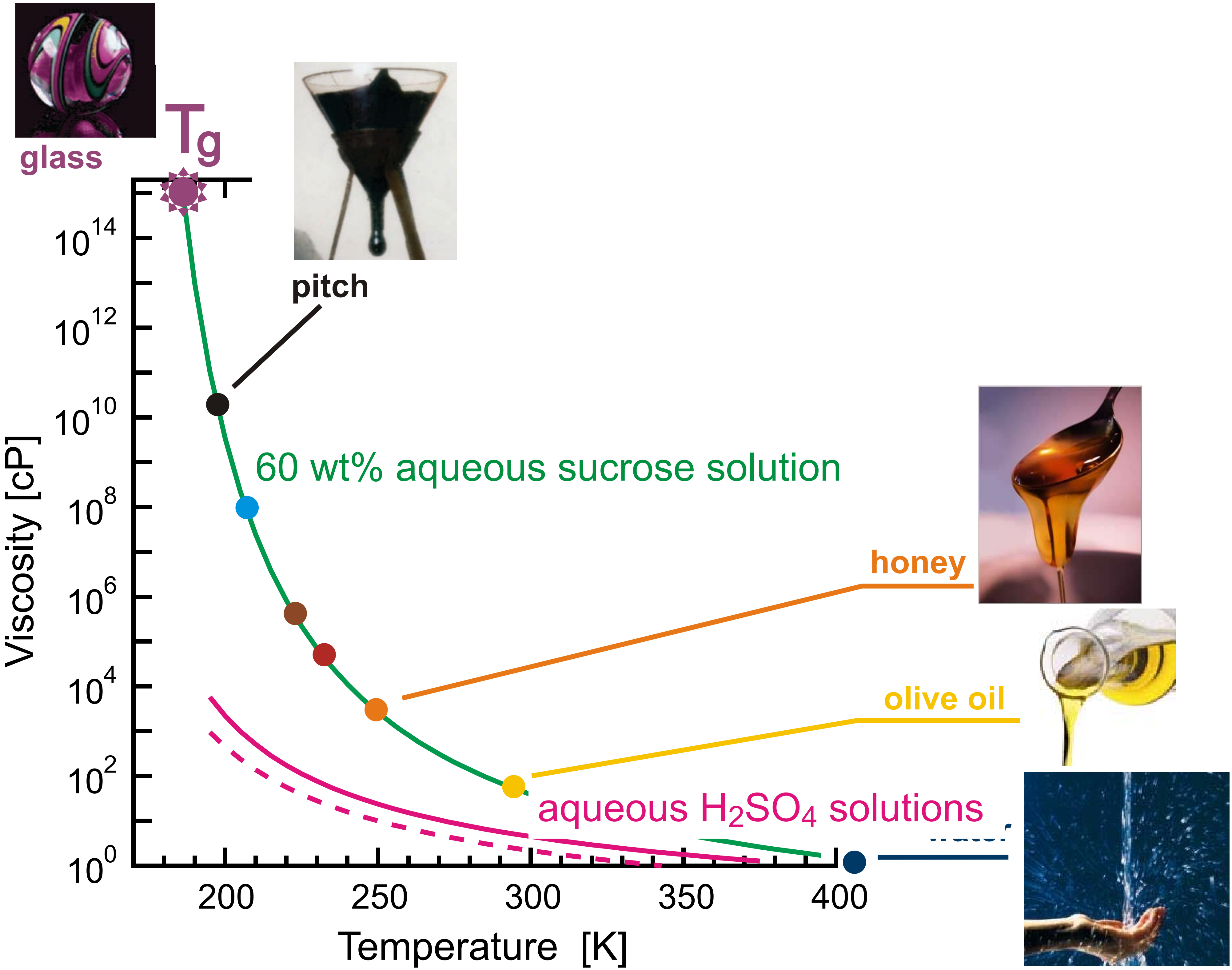
Temperature [K]



glass
T_g
pitch
window putty
peanut butter
ketchup
honey
olive oil
water
Viscosity [cP]
10^{0}
10^{2}
10^{4}
10^{6}
10^{8}
10^{10}
10^{12}
10^{14}
200
250
300
350
400
Temperature [K]



glass
Tg
pitch
60 wt% aqueous sucrose solution
honey
olive oil
water
Viscosity [cP]
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
10^{4}
10^{2}
10^{0}
200
250
300
350
400
Temperature [K]



glass
Tg
pitch
60 wt% aqueous sucrose solution
honey
olive oil
aqueous H_2SO_4 solutions
Viscosity [cP]
10^{14}
10^{12}
10^{10}
10^{8}
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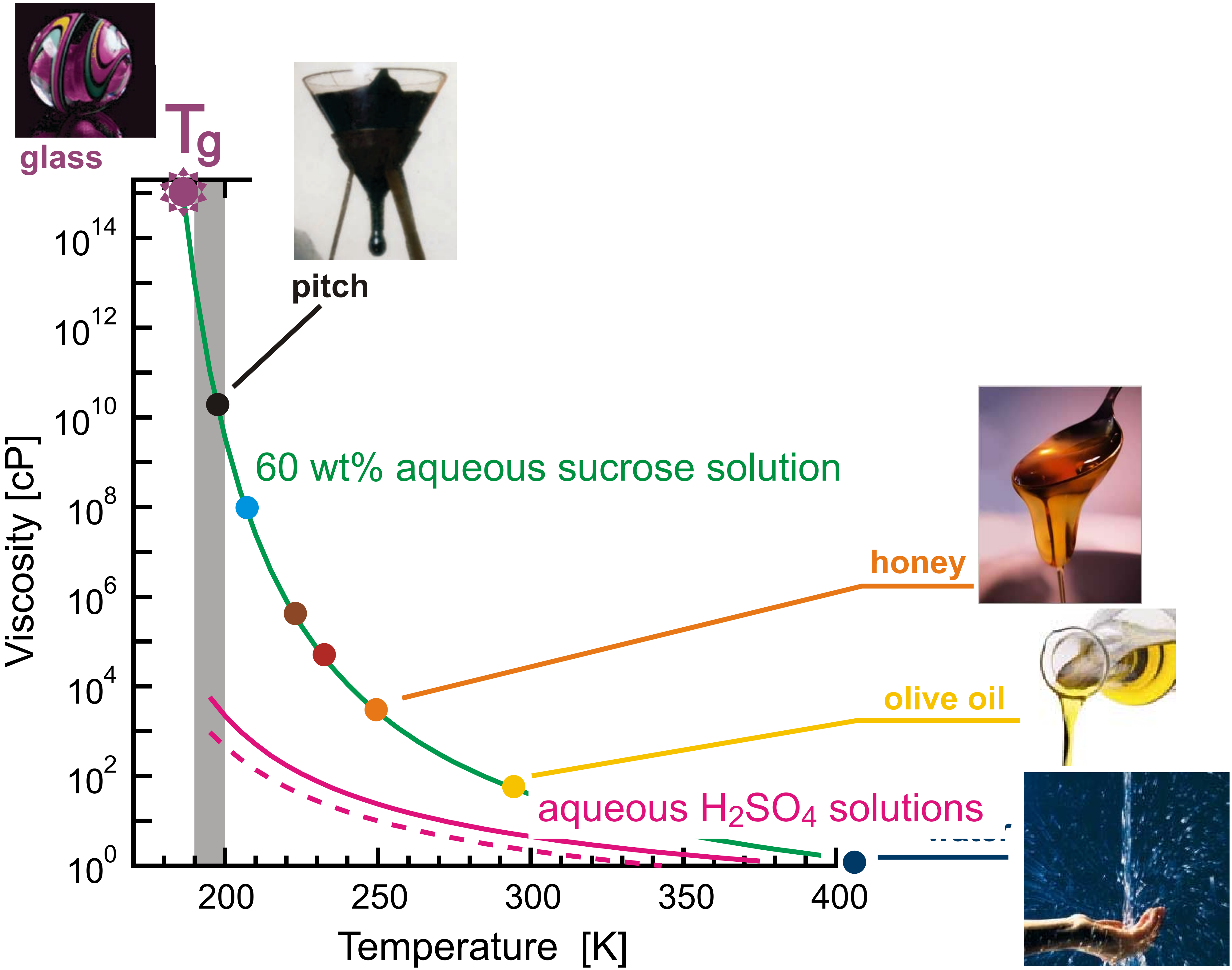
glass
Tg
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aqueous H2SO4 solutions
Viscosity [cP]
10^14
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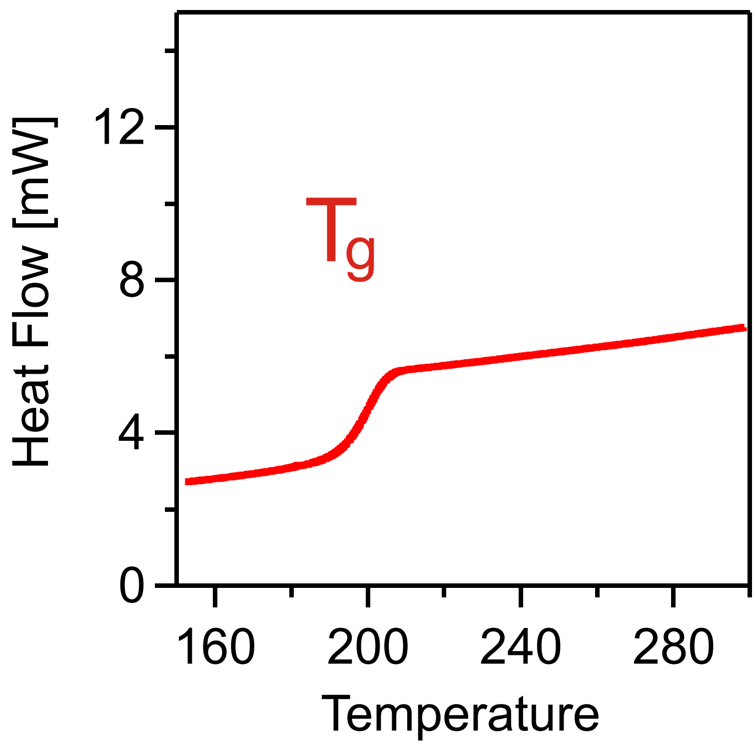
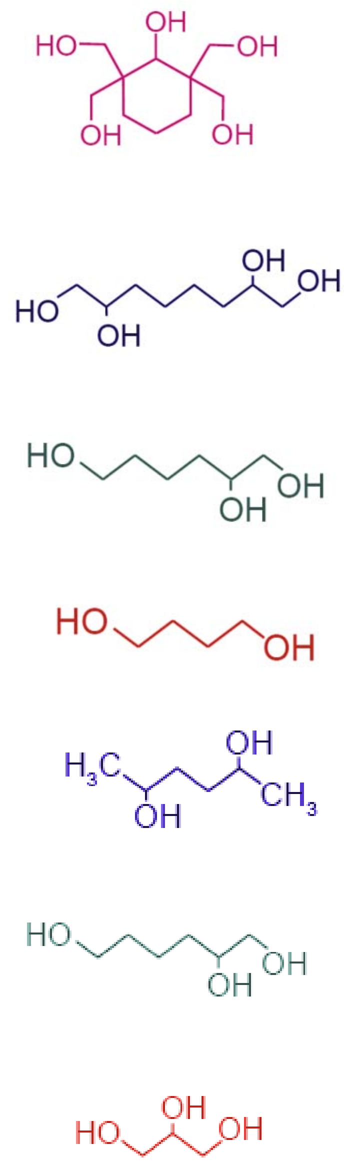
10^8
10^6
10^4
10^2
10^0
200
250
300
350
400
Temperature [K]

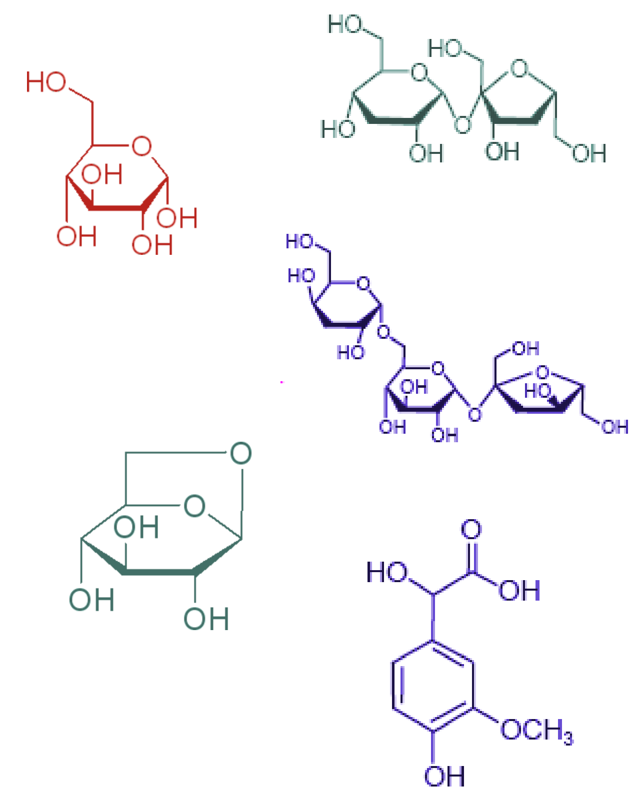
Experimental Determination of Glass Transition Temperature

Differential Scanning Calorimetry



Various binary organic systems



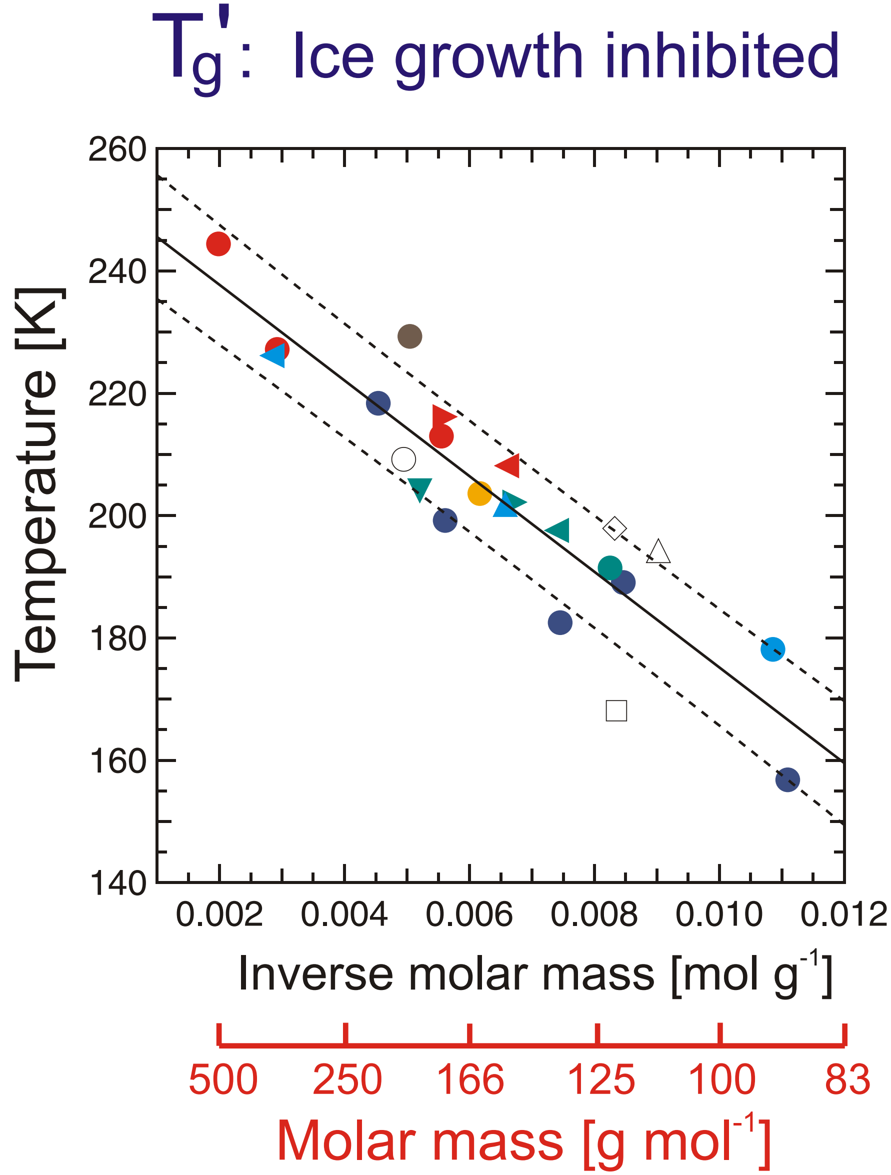


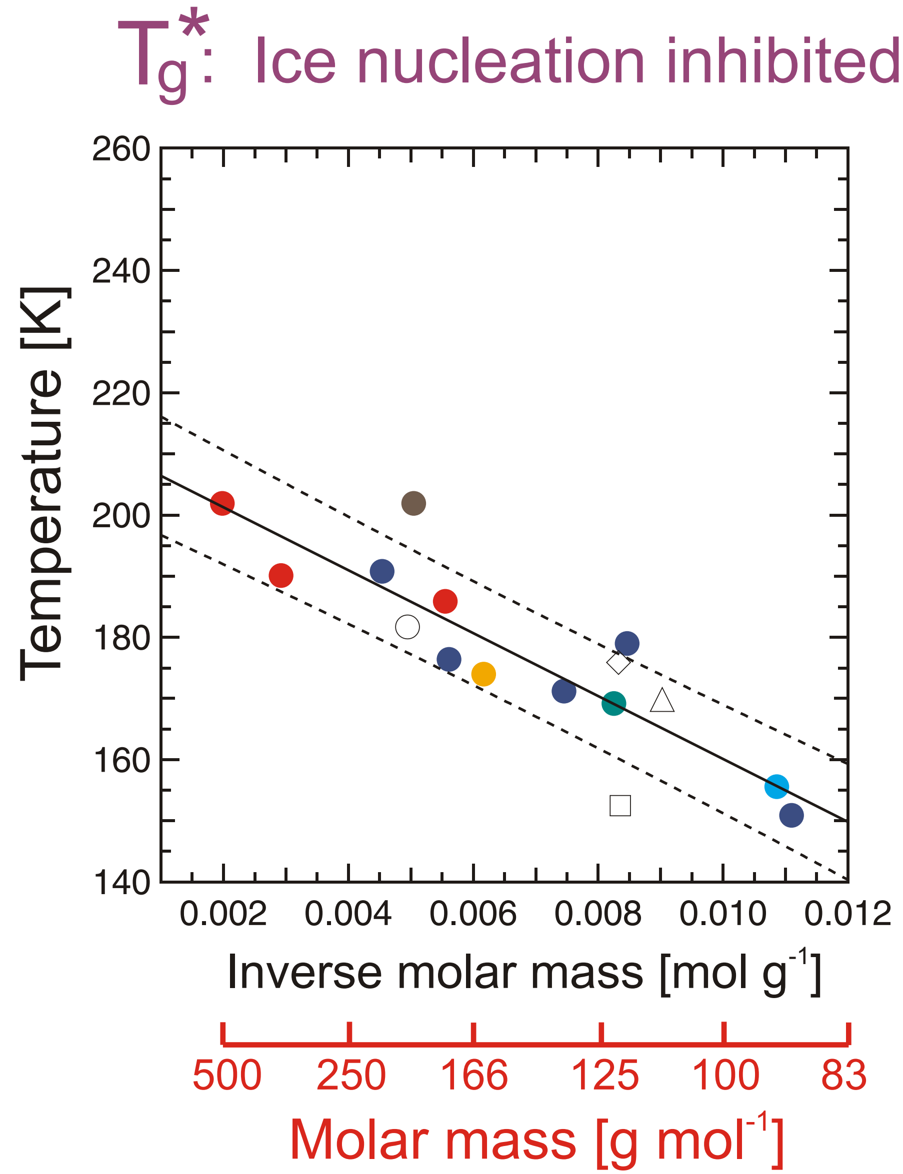
Various multicomponent systems:

organic / organic
organic / inorganic

Zobrist et al., ACP 2008

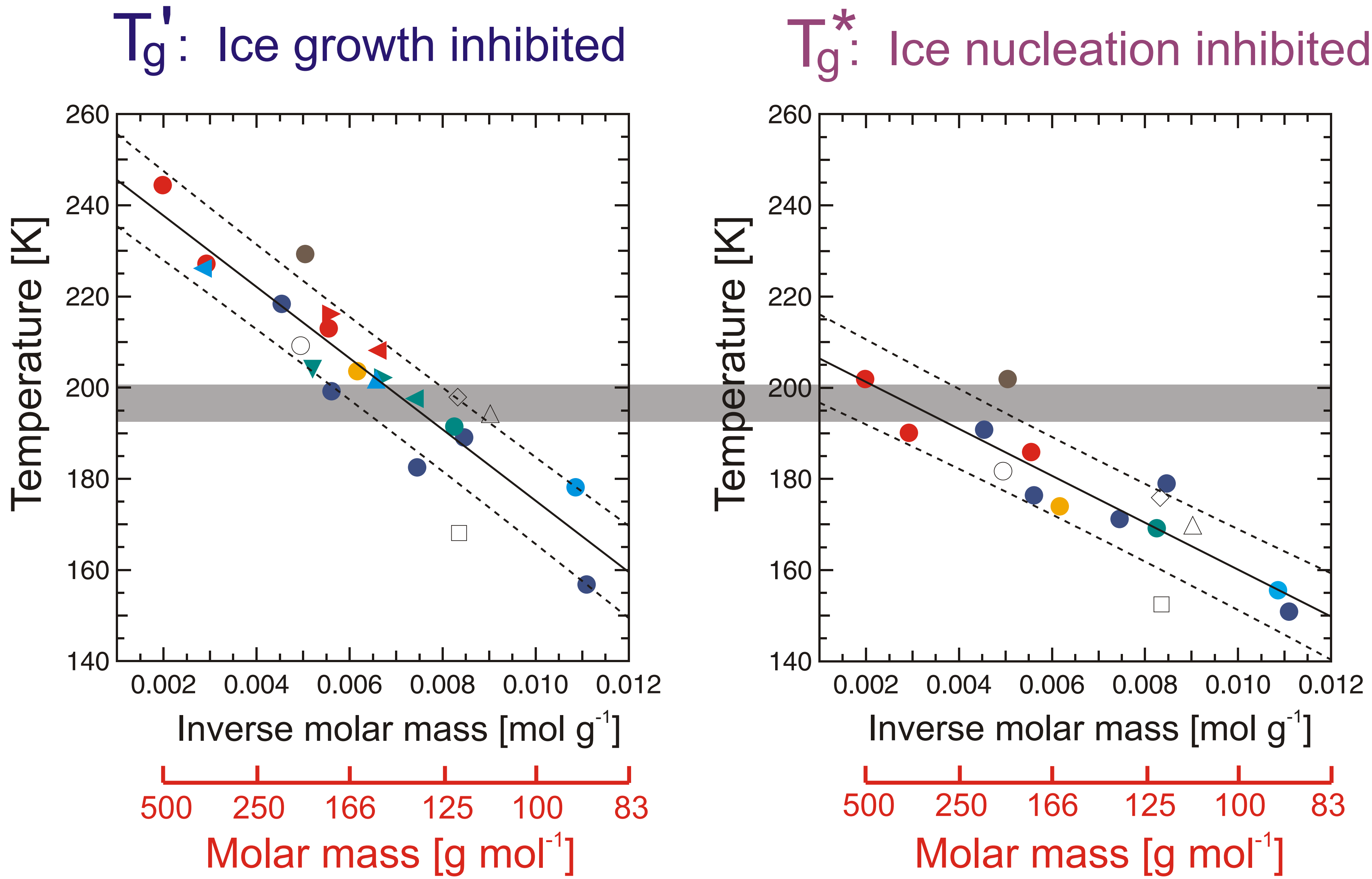
Tg dependence on molar mass of organic





Zobrist et al., ACP 2008

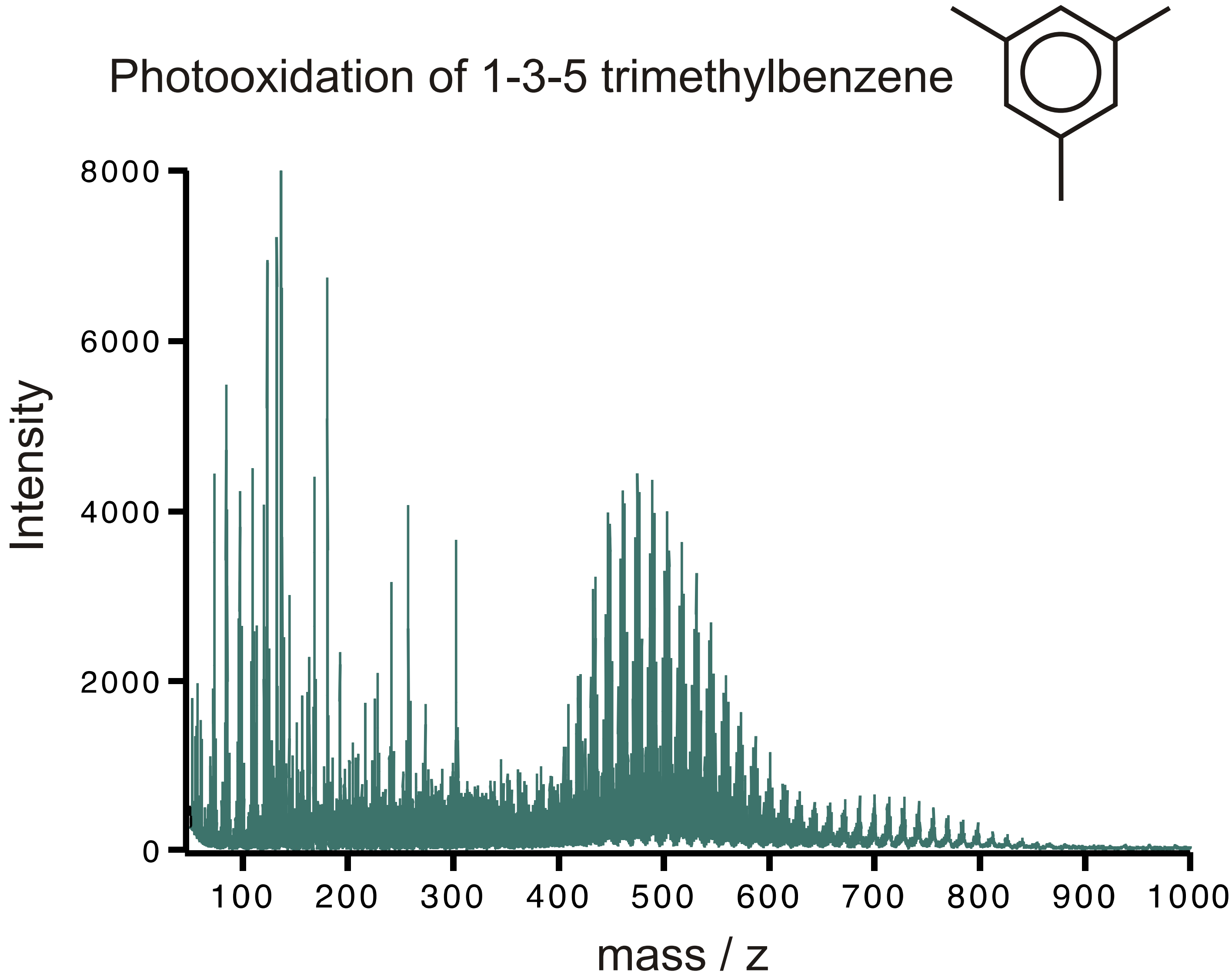
Tg dependence on molar mass of organic



Zobrist et al., ACP 2008

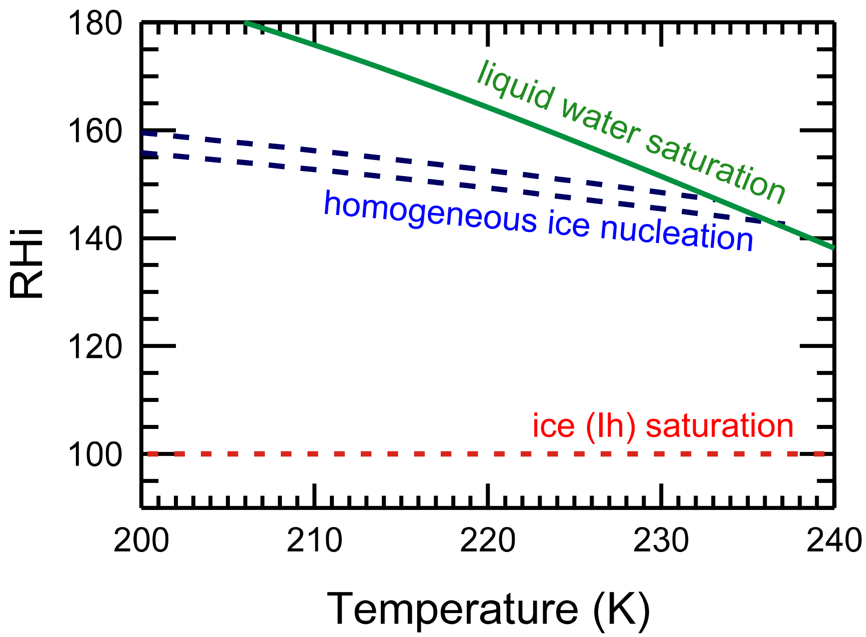
Polymers in Secondary Organic Aerosols

Photooxidation of 1-3-5 trimethylbenzene



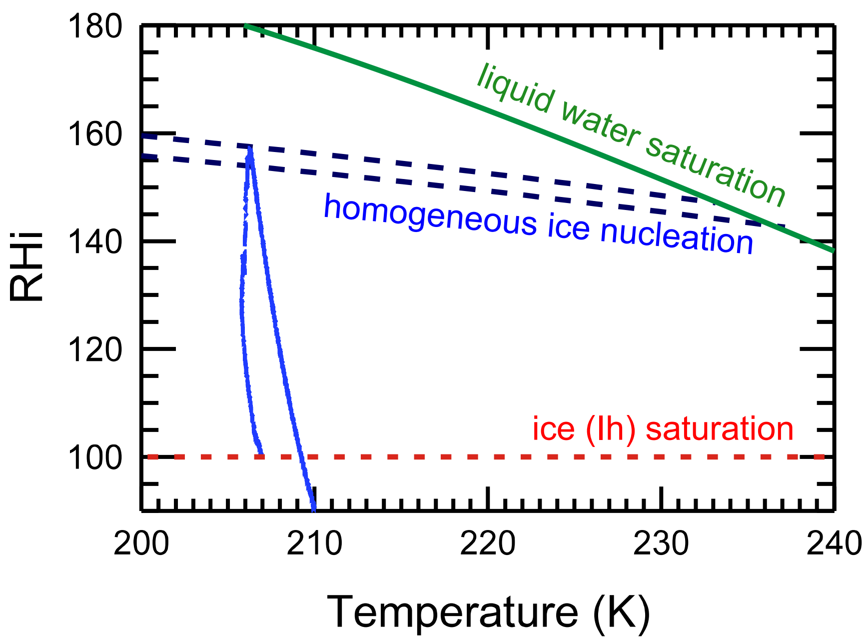
Kalberer et al, Science 2004

Ice nucleation studies in AIDA chamber



Ice nucleation studies in AIDA chamber

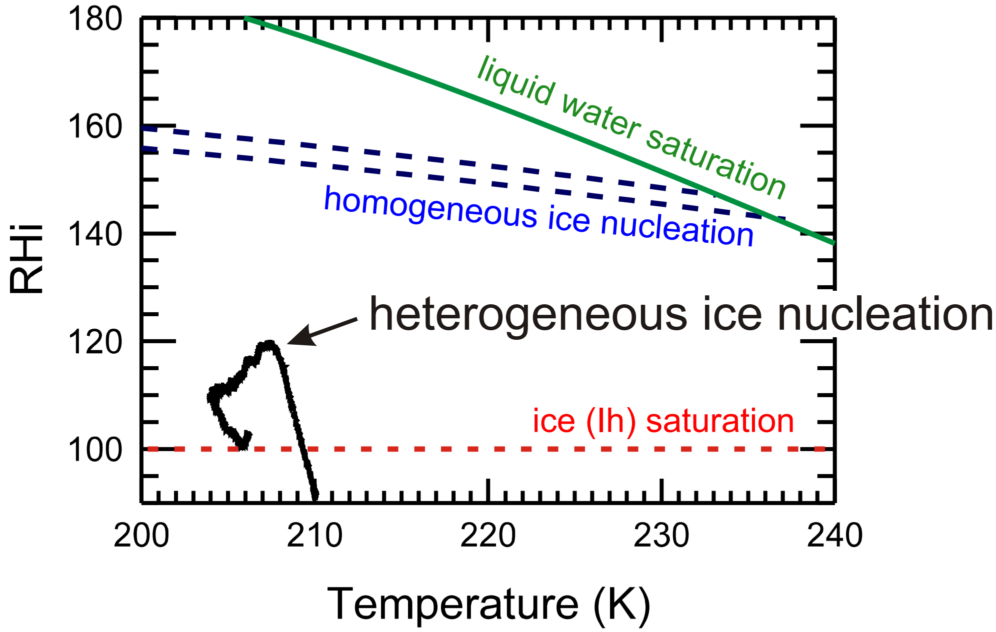
H2SO4 particles 



Ice nucleation studies in AIDA chamber

Möhler et al, ERL 2008

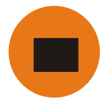
illite particles

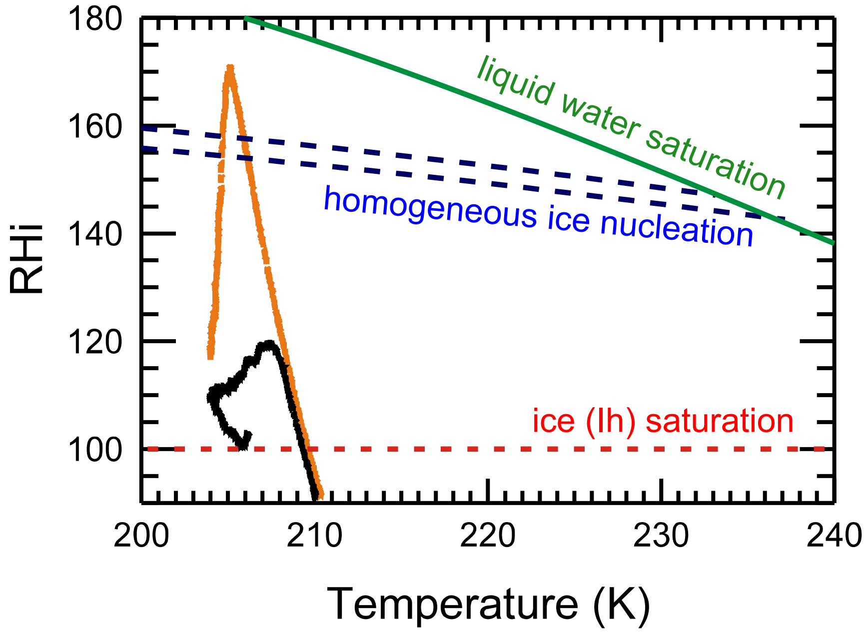


Ice nucleation studies in AIDA chamber

Möhler et al, ERL 2008

illite particles 

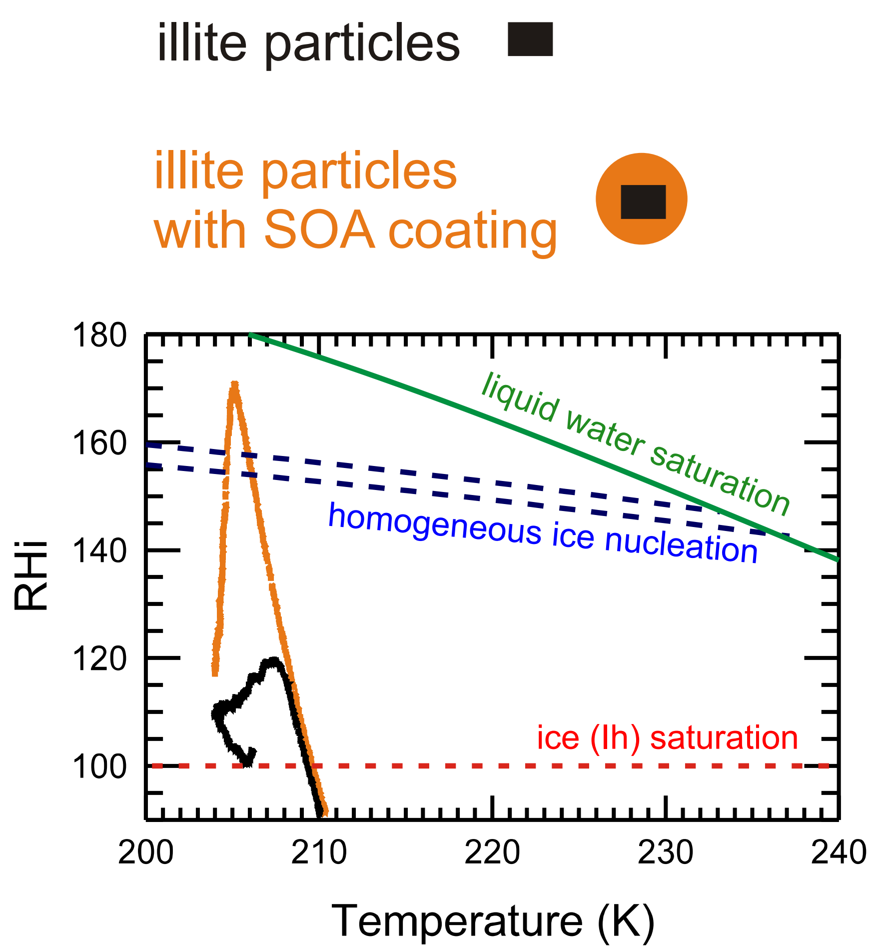
illite particles
with SOA coating 

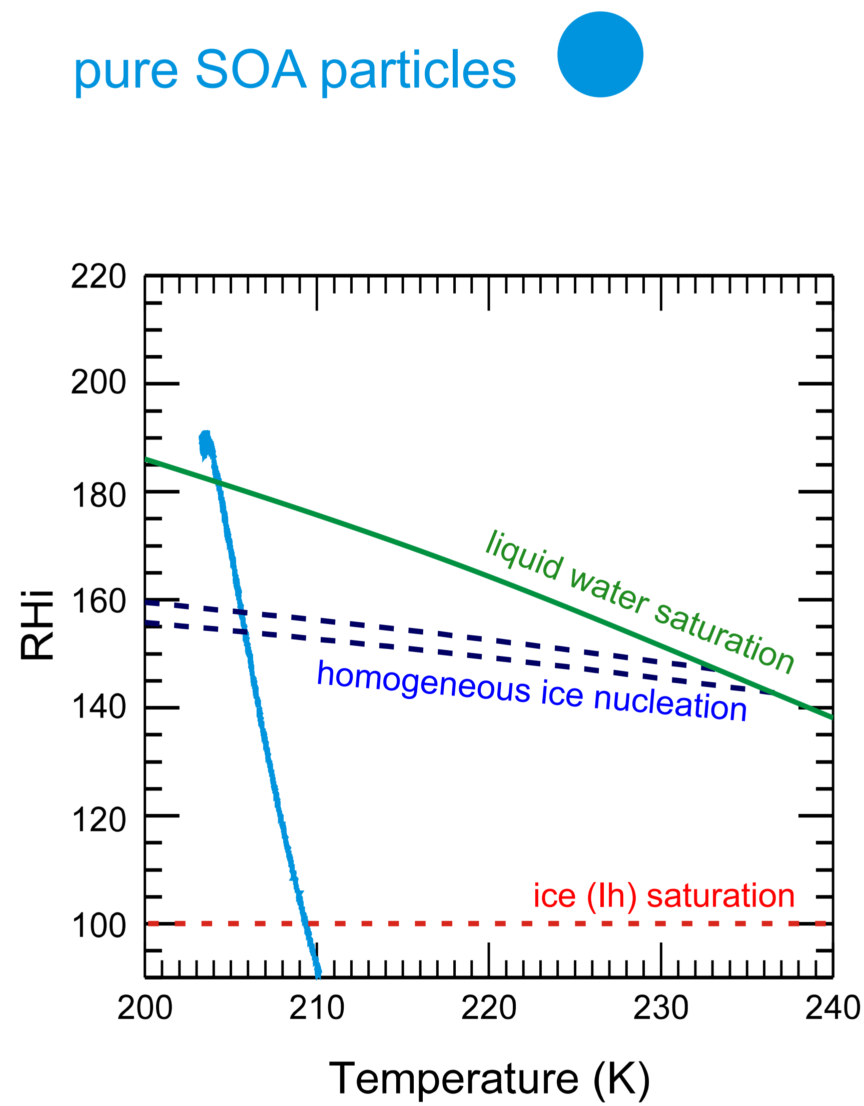


=> heterogeneous ice nucleation
is inhibited by SOA coating

Ice nucleation studies in AIDA chamber

Möhler et al, ERL 2008





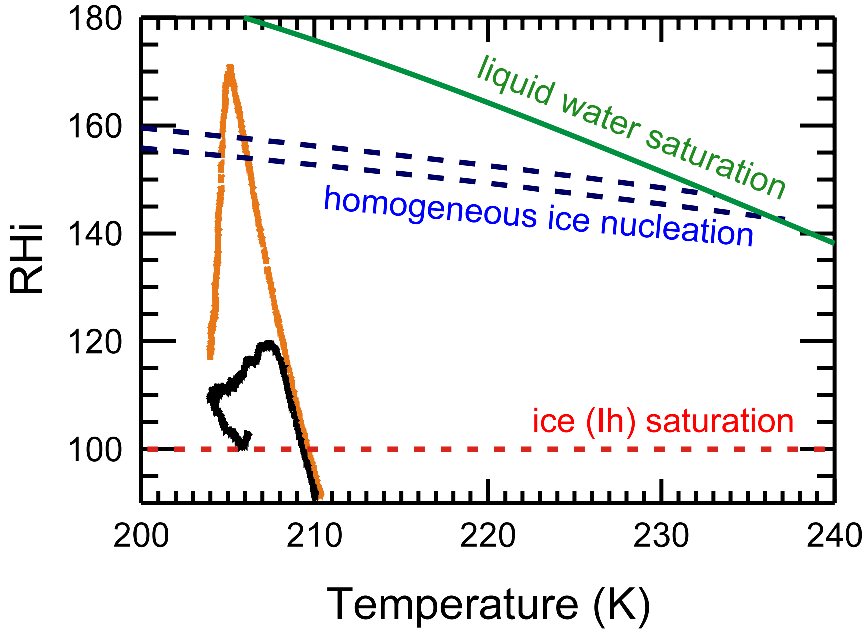
=> heterogeneous ice nucleation is inhibited by SOA coating

Ice nucleation studies in AIDA chamber

Möhler et al, ERL 2008

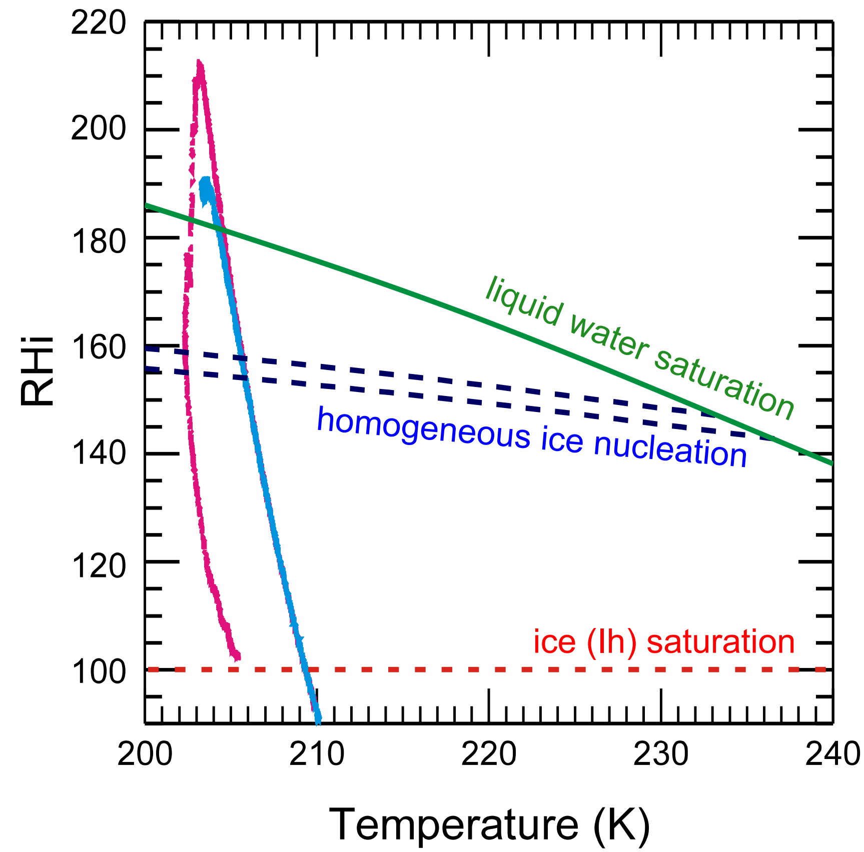
illite particles

illite particles
with SOA coating



pure SOA particles

second cycle with faster expansion



=> heterogeneous ice nucleation is inhibited by SOA coating

=> homogeneous ice nucleation is strongly inhibited in SOA

Potential solutions to the clear-air puzzle

- Measurement uncertainties? probably not large enough
- Small α_m of water on nucleating ice crystals? unlikely
- Glass forming aerosols? likely candidate

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Glass formation in aqueous organic aerosol particles

- Depends primarily on molar mass of solutes ($M_W > 150$ g mol^{-1})
- Inhibition of water uptake and heterogeneous chemistry
- Inhibition of ice nucleation and growth

See Poster P111 by Zobrist

=> Enhanced lifetime of organic aerosols