Solid ammonium nitrate aerosols as efficient ice nucleating particles in the upper troposphere during Asian monsoons: aircraft, satellite and cloud-chamber investigations

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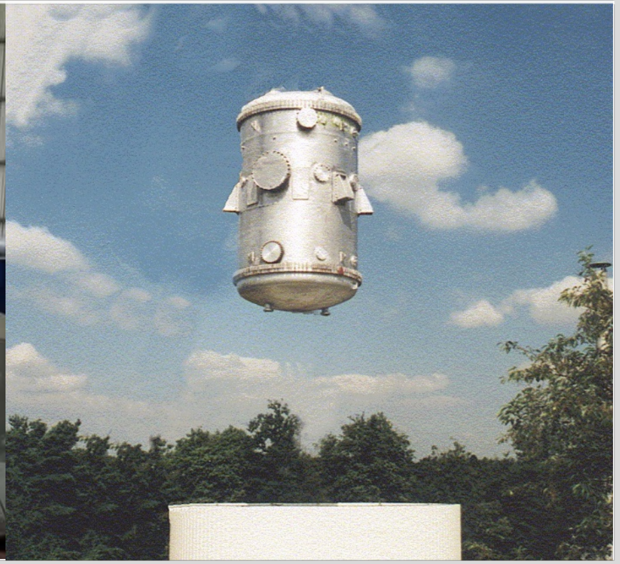


The ATAL

CALIPSO detection of an Asian tropopause aerosol layer

J.-P. Vernier,[1] L. W. Thomason,[1] and J. Kar[2]

GRL, 2011, 10.1029/2010GL046614

Increase in upper tropospheric and lower stratospheric aerosol levels and its potential connection with Asian pollution

J.-P. Vernier[1,2], T. D. Fairlie[2], M. Natarajan[2], F. G. Wienhold[3], J. Bian[4], B. G. Martinsson[5], S. Crumeyrolle[6], L. W. Thomason[2], and K. M. Bedka[2]

JGR, 2014, 10.1002/2014JD022372

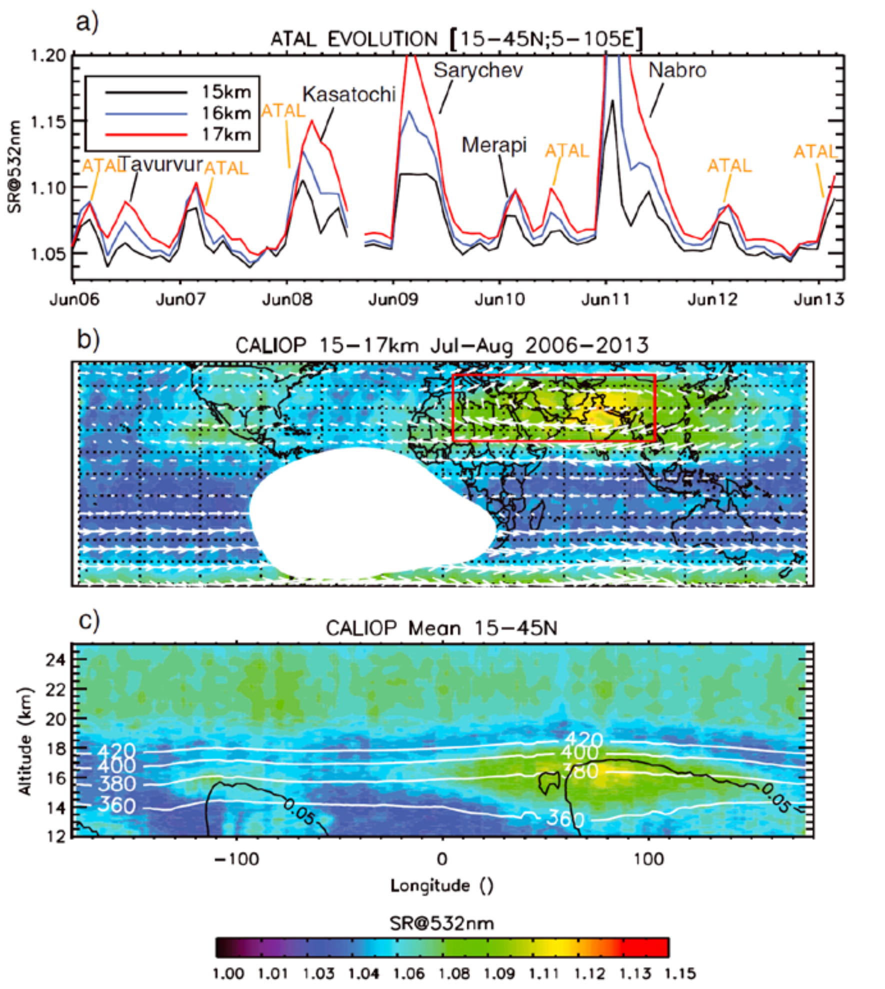


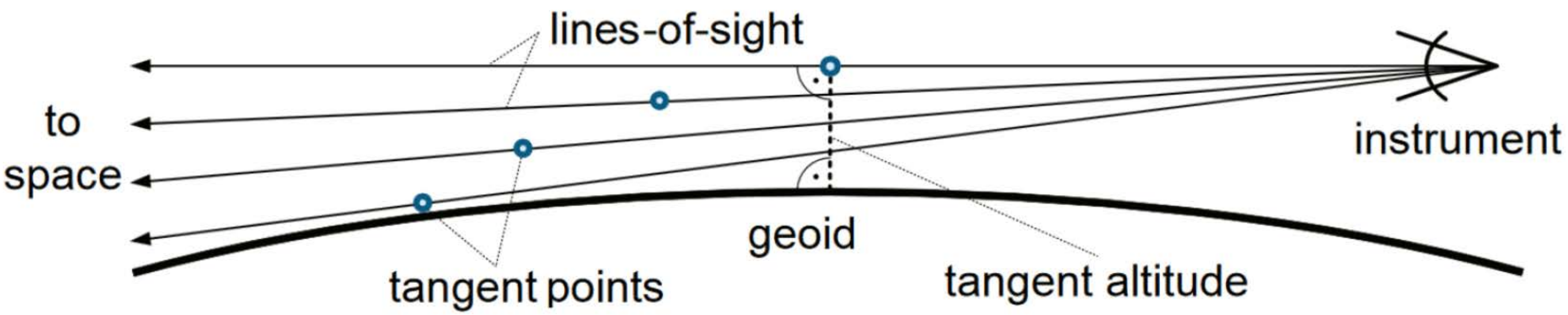
Fig. 2, Vernier et al., JGR, 2014, 10.1002/2014JD022372

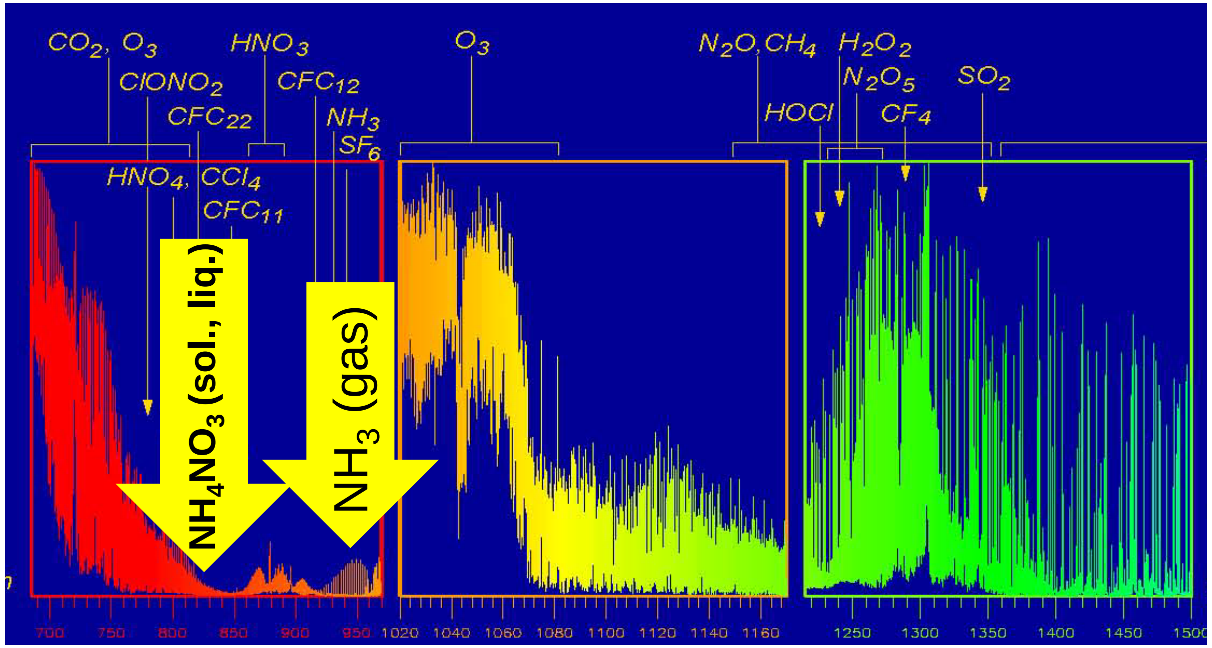
ATAL has a direct aerosol radiative effect of:
“-0.1 W/m^2 in the past 18 years.” (Vernier et al., 2014, 10.1002/2014JD022372)

Questions:

- **What is the composition and phase of ATAL particles?**
- **What is their source?**
- ***Can ATAL particles influence nucleation of cirrus clouds and, thus, have an indirect radiative effect possibly larger than the direct one?***

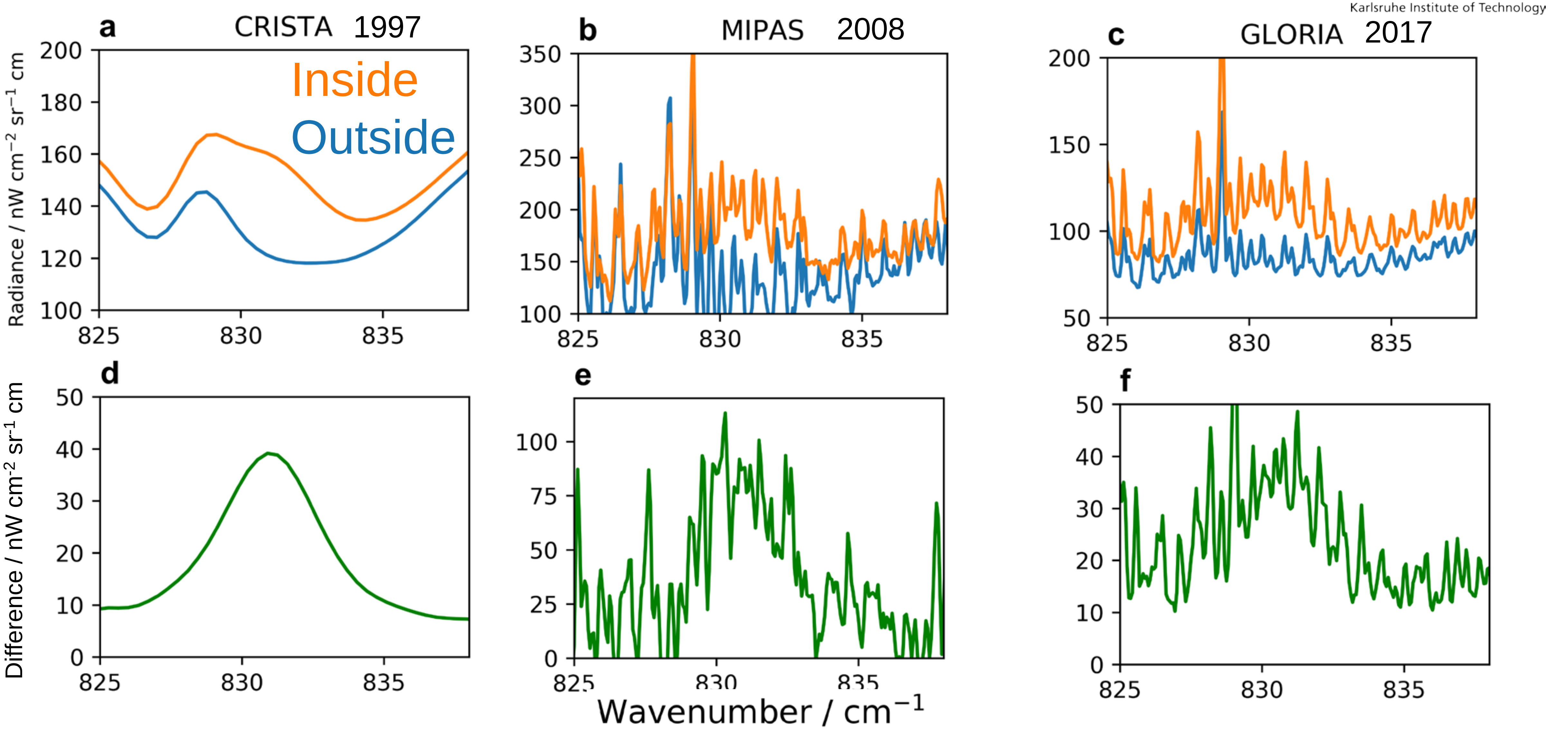
Infrared limb sounding to investigate composition/phase/origin of the ATAL





13 µm 7 µm

- A spectral band at 831 cm^{-1} was detected in infrared spectra of satellite (CRISTA, MIPAS) and airborne (GLORIA) instruments only inside the monsoon upper troposphere



Höpfner et al., Nat. Geosci, 2019,
10.1038/s41561-019-0385-8, suppl. Fig. 4

- The AIDA aerosol and cloud chamber was used to measure infrared spectra of solid and liquid ammonium nitrate particles at upper tropospheric temperatures

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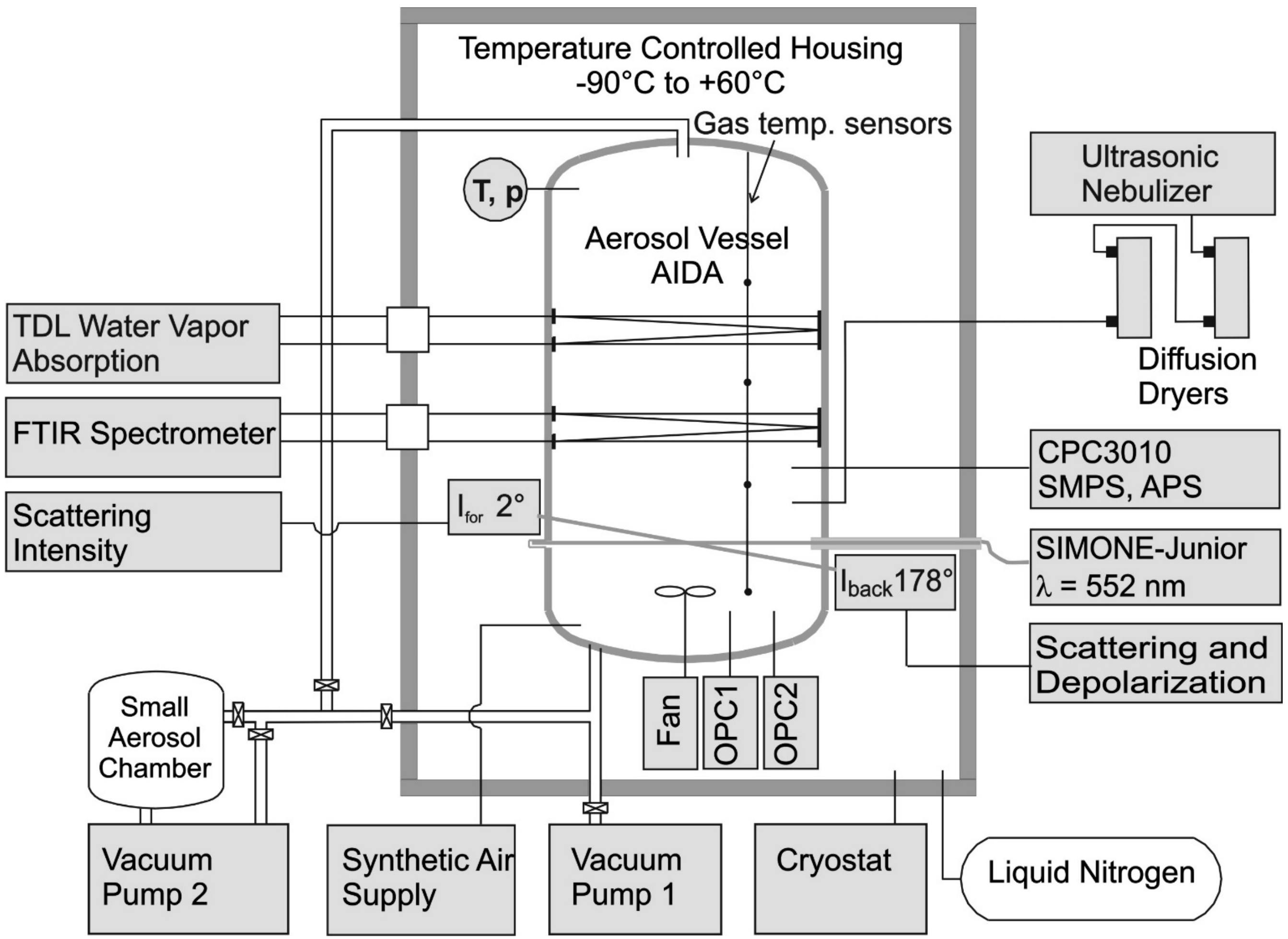

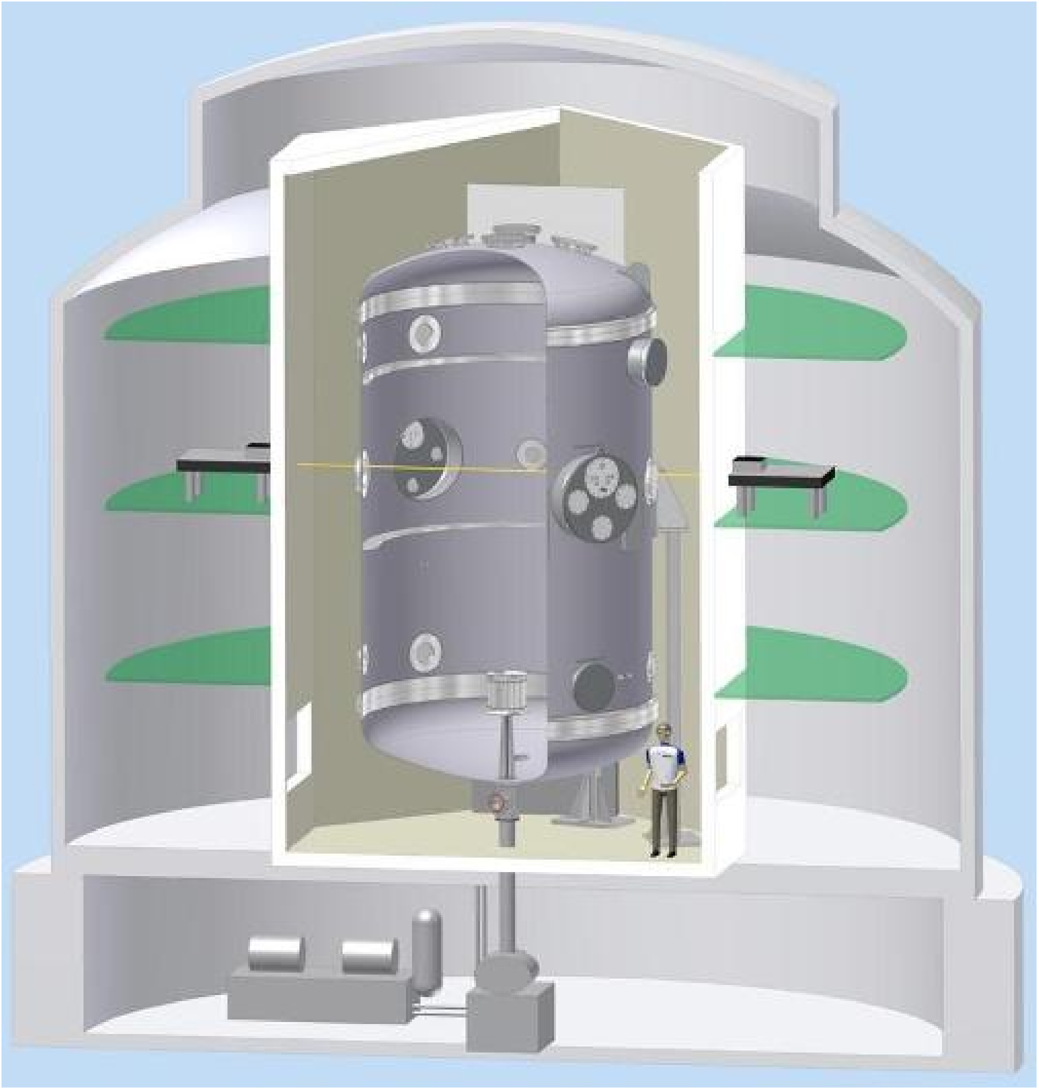

Laboratory infrared spectra of the $\nu_2(NO_3^-)$ band of NH_4NO_3 particles compared to the observations

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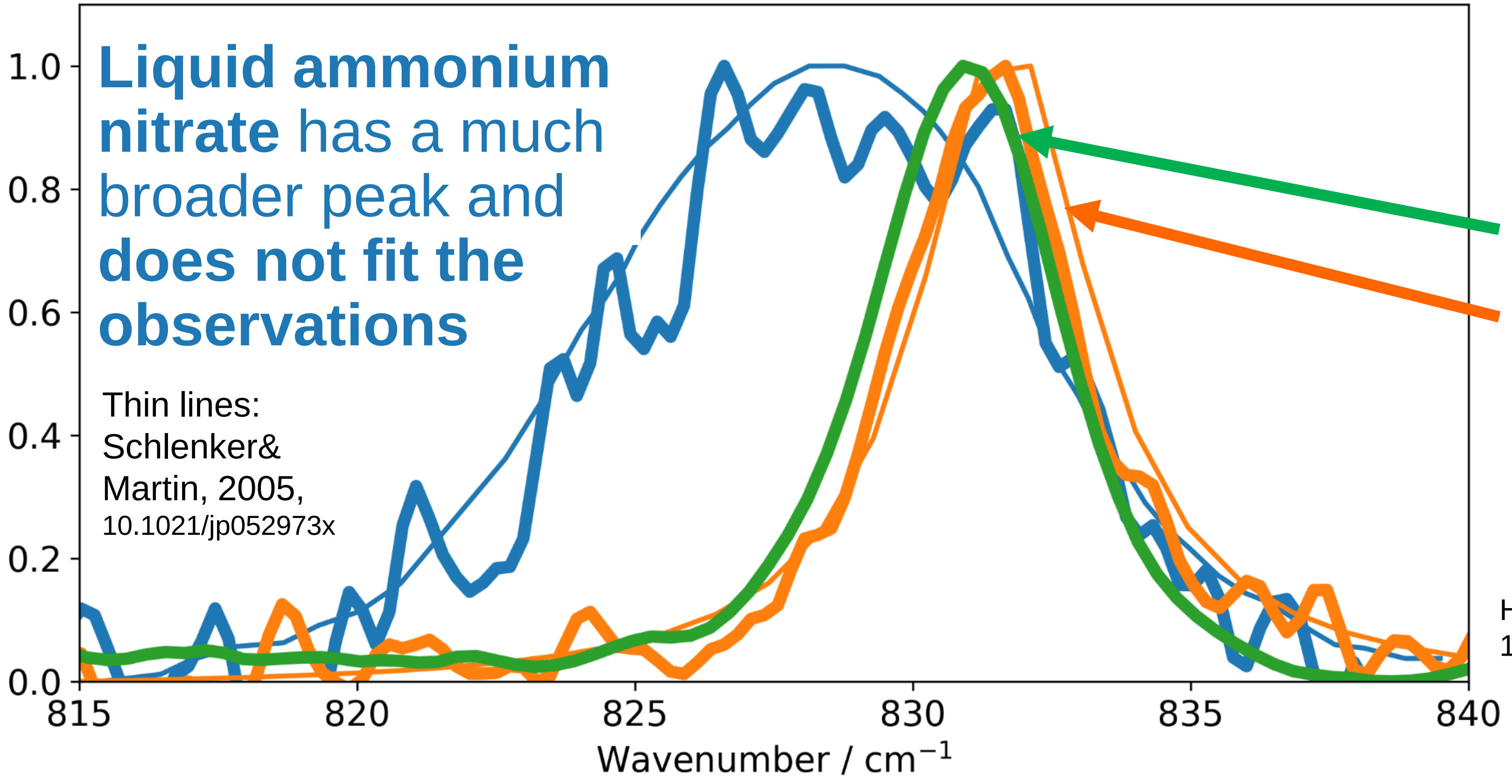


Höpfner et al., Nat. Geosci, 2019,
10.1038/s41561-019-0385-8, suppl. Fig. 1

- **Laboratory observations show that the infrared signature is due to solid ammonium nitrate particles**
- **Solid AN particles only form when impurities of ammonium sulfate are present**
- **This allows to derive ammonium nitrate mass concentration profiles from the infrared limb observations**

The StratoClim campaign 2017:
the first high-altitude aircraft measurements in the Asian monsoon upper troposphere

Russian M55 Geophysica research aircraft

- Altitude up to 21 km
- Range up to 4000 km

Basis: Kathmandu (Nepal)

July and August 2017

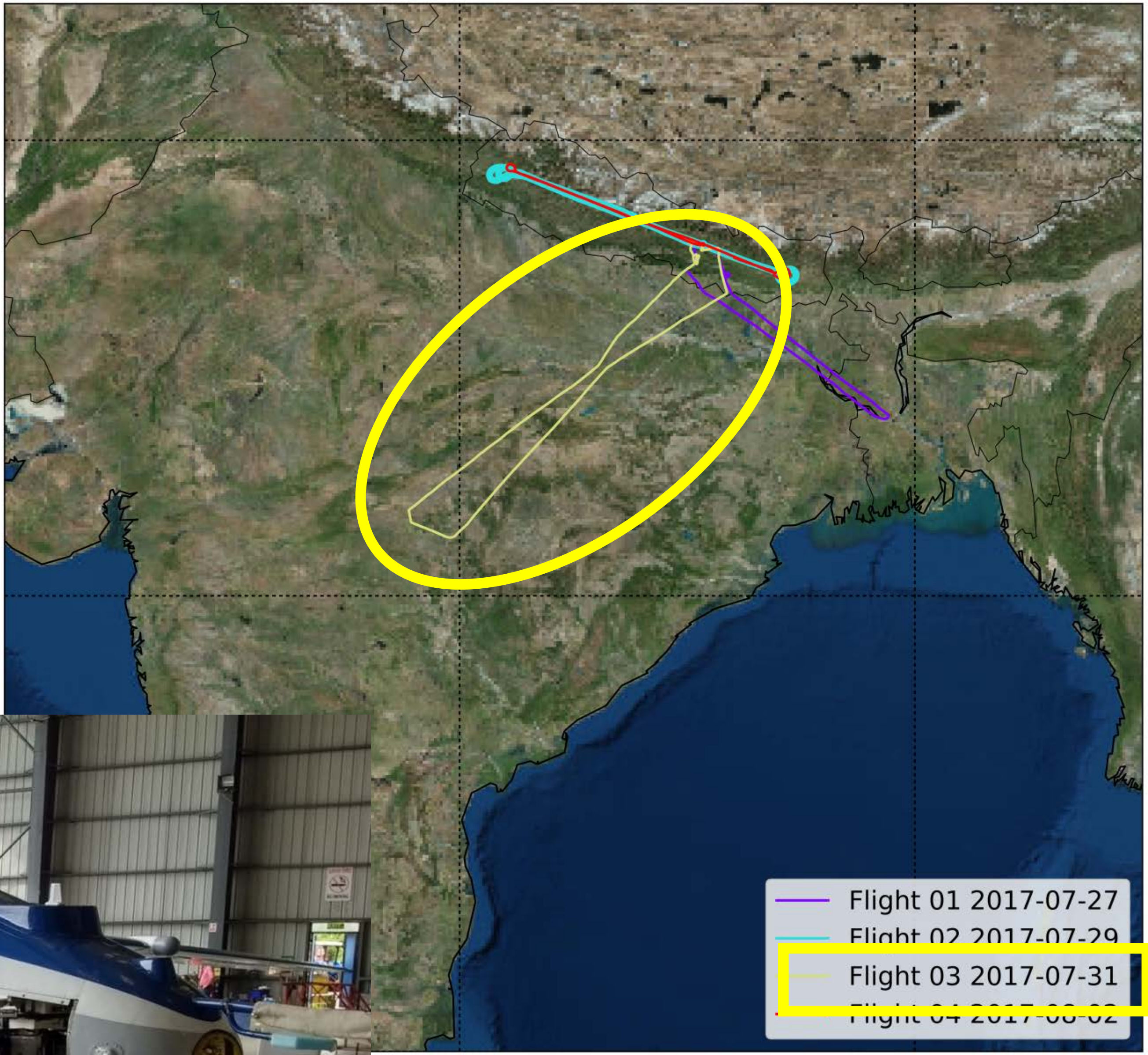
8 local research flights (4 with GLORIA on board)

Simultaneous measurements:

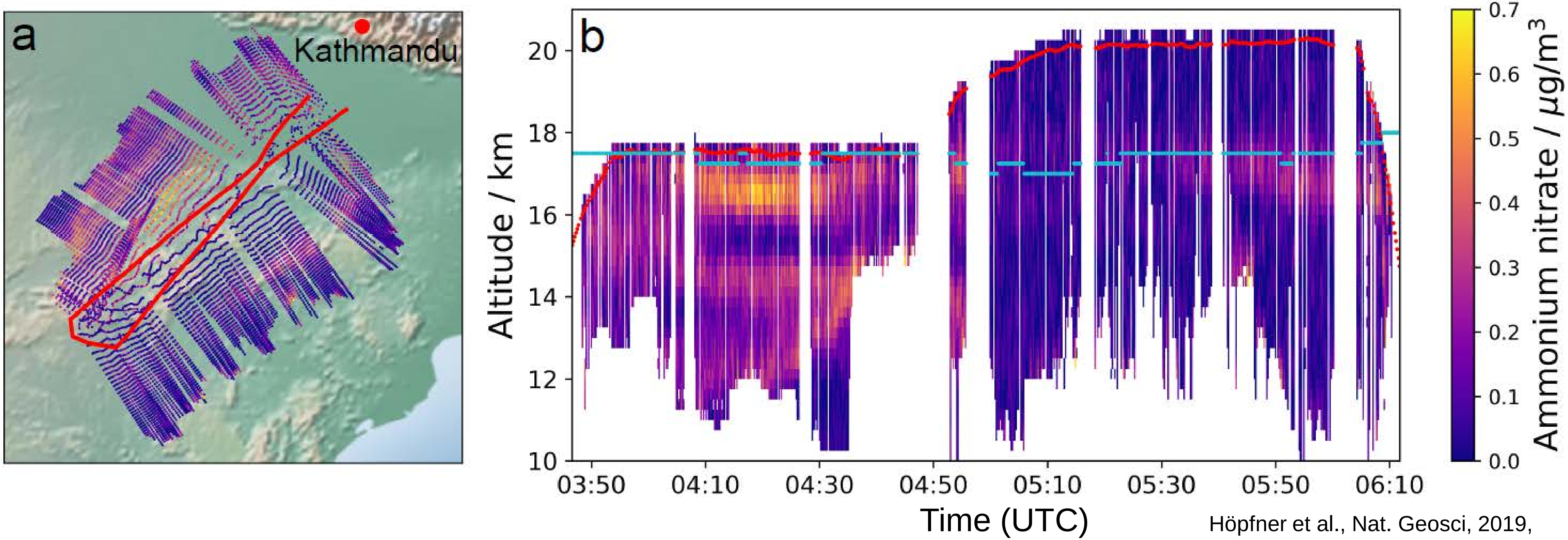
- **GLORIA IR-limb sounder**

- **In-situ particle instruments (size distribution, composition)**

StratoClim GLORIA flight tracks



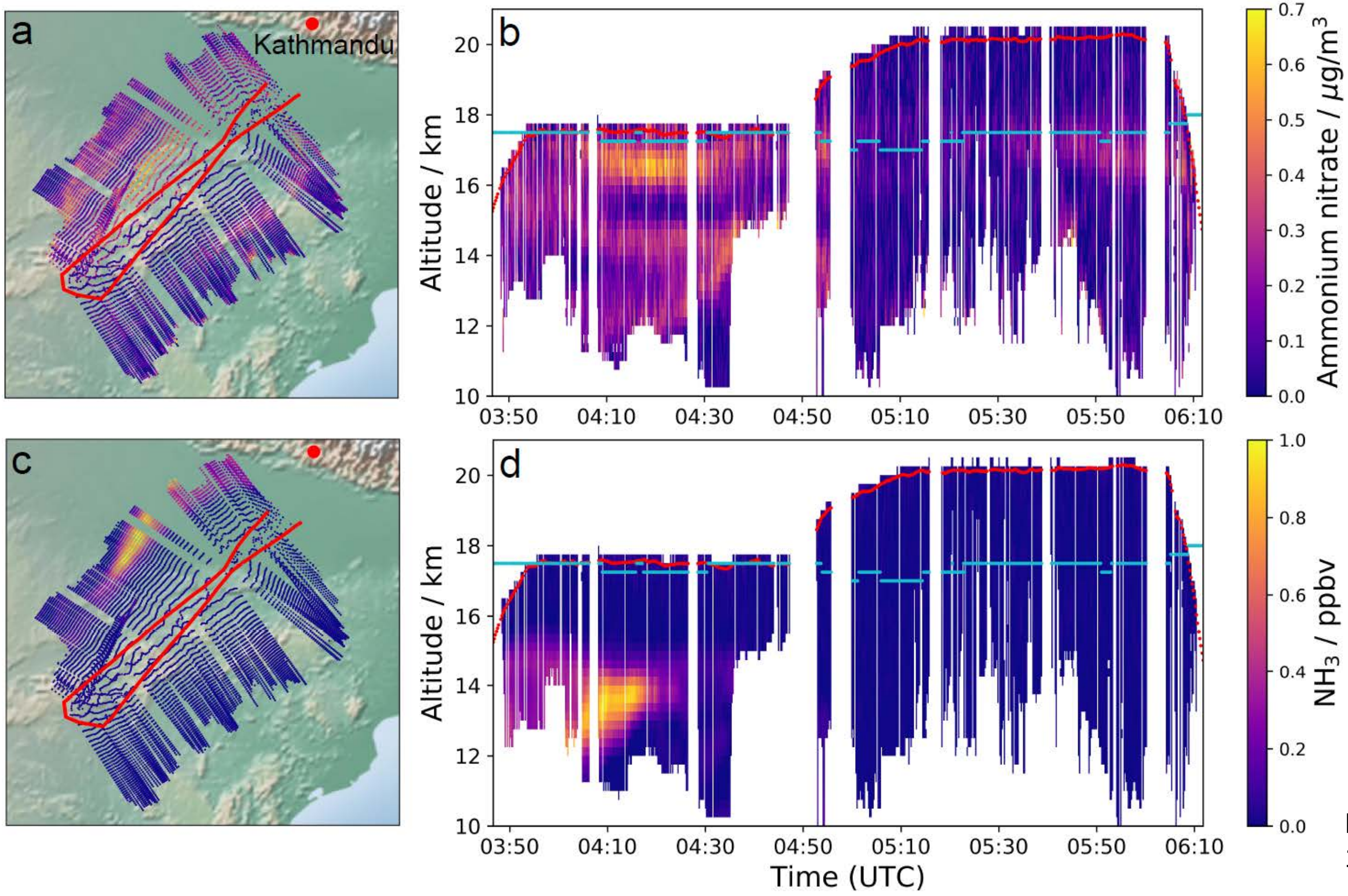
StratoClim flight 31 Jul 2017
Ammonium nitrate aerosol mass density



Höpfner et al., Nat. Geosci, 2019, 10.1038/s41561-019-0385-8, Fig. 3

- **Ammonium nitrate layers near the tropopause and at 12-14 km**
- **Higher concentrations in NW-direction**

StratoClim flight 31 Jul 2017



NH_4NO_3 aerosol mass density

NH_3 trace gas mixing ratio

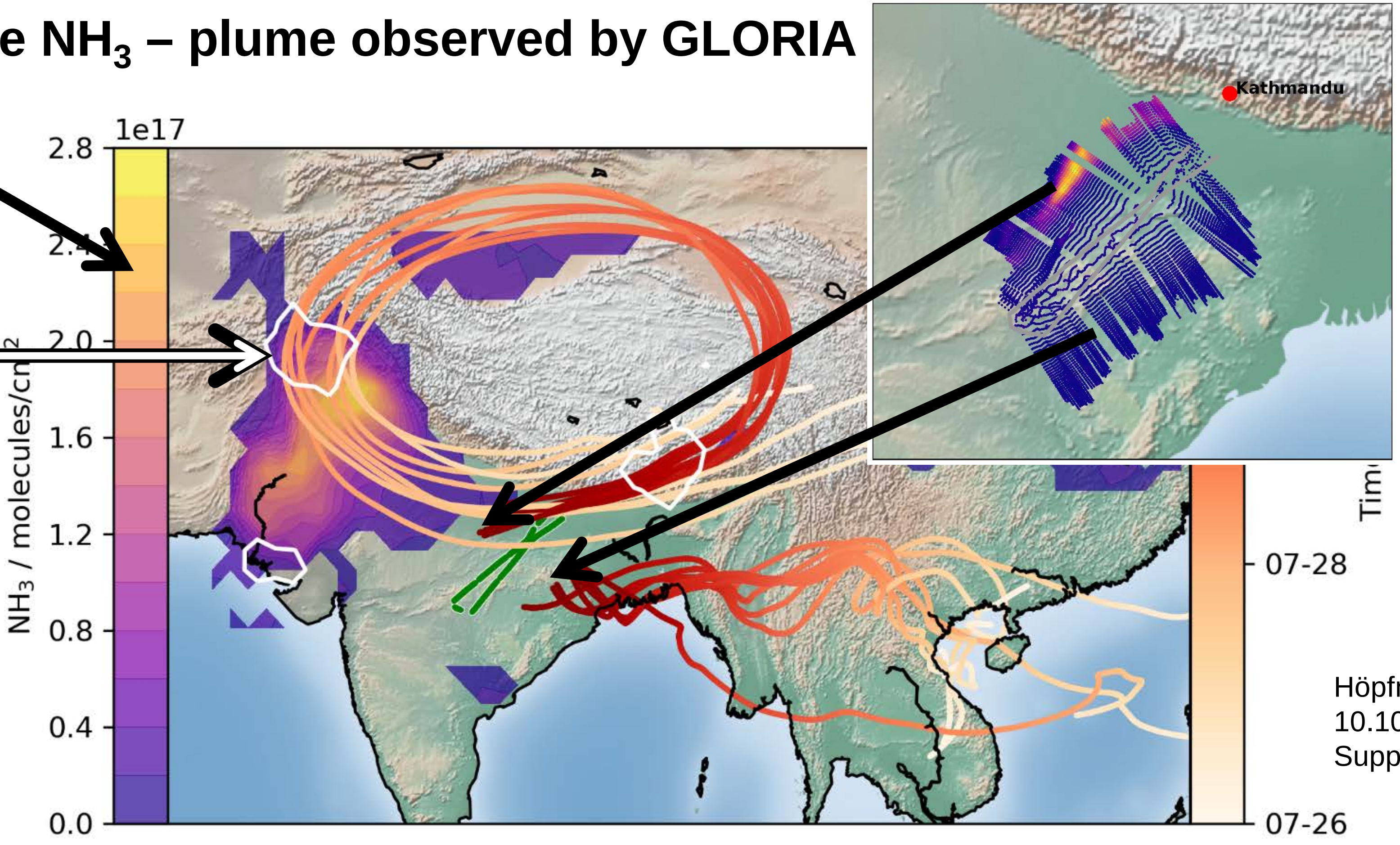
Höpfner et al., Nat. Geosci, 2019, 10.1038/s41561-019-0385-8, Fig. 3

- Large concentrations of NH_3 observed at 14 km
- Enhanced ammonium nitrate in the vicinity of regions with enhanced NH_3

Origin of the NH_3 – plume observed by GLORIA

IASI NH_3 (low-mid troposphere)

Density of convective events along backward trajectories



http://iasi.aeris-data.fr/NH3
The data produced at Université Libre de Bruxelles (ULB) by Simon Whitburn and Martin Van Damme
Van Damme et al., AMT, 2017

Höpfner et al., Nat. Geosci, 2019, 10.1038/s41561-019-0385-8, Suppl. Fig. 10

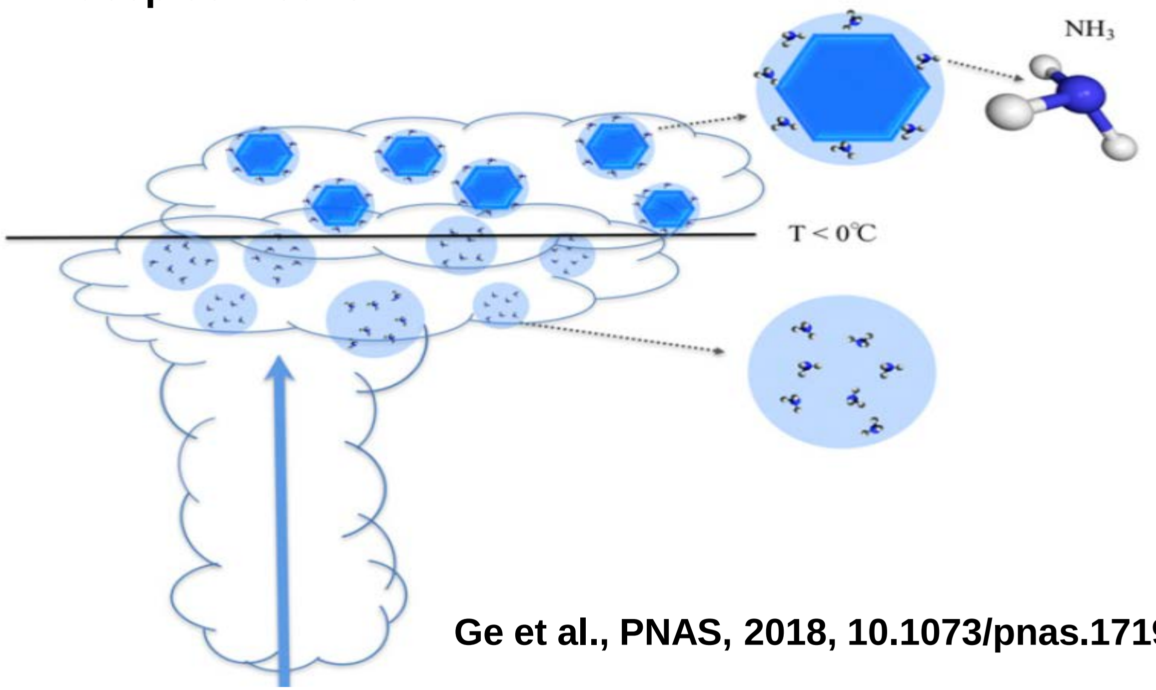
➢ **High NH_3 at 14 km altitude traced back to regions with strong convection and with enhanced concentrations of NH_3 in the lower troposphere as detected by the IASI infrared nadir sounder**

Why is NH_3 not washed out during convection?

A molecular perspective for global modeling of upper atmospheric NH_3 from freezing clouds

Cui Ge[a,1], Chongqin Zhu[b,1], Joseph S. Francisco[b,2], Xiao Cheng Zeng[b,2], and Jun Wang[a,2]

- Study trying to explain the MIPAS observations of high concentrations of NH_3 in the upper troposphere
- "We show that the NH_3 dissolved in liquid cloud droplets is prone to being released into the UTLS upon freezing during deep convection."



Ge et al., PNAS, 2018, 10.1073/pnas.1719949115

?

- ph – dependence of NH_3 solubility in liquid water: „Convective clouds are hardly acidic so that NH_3 is only partly dissolved and removed by precipitation"

Metzger et al., JGR, 2002, 10.1029/2001JD001103

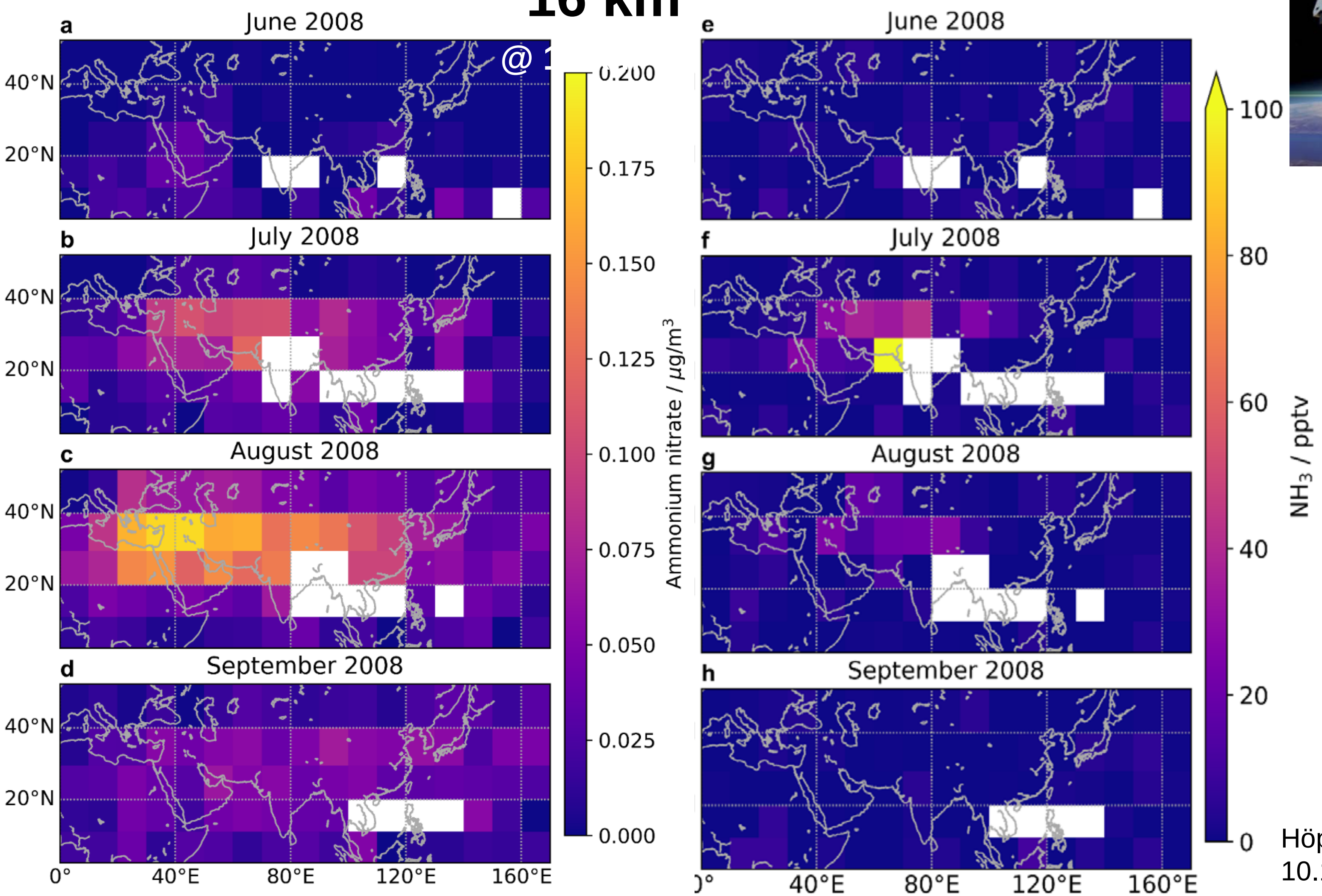
➢ It is still an open question, which of these processes (or a different one) is responsible for NH_3 not being completely washed/rained out during convection but reaching the upper troposphere.

MIPAS/Envisat observations

NH_4NO_3 aerosol mass density

2008
16 km

NH_3 gas mixing ratio



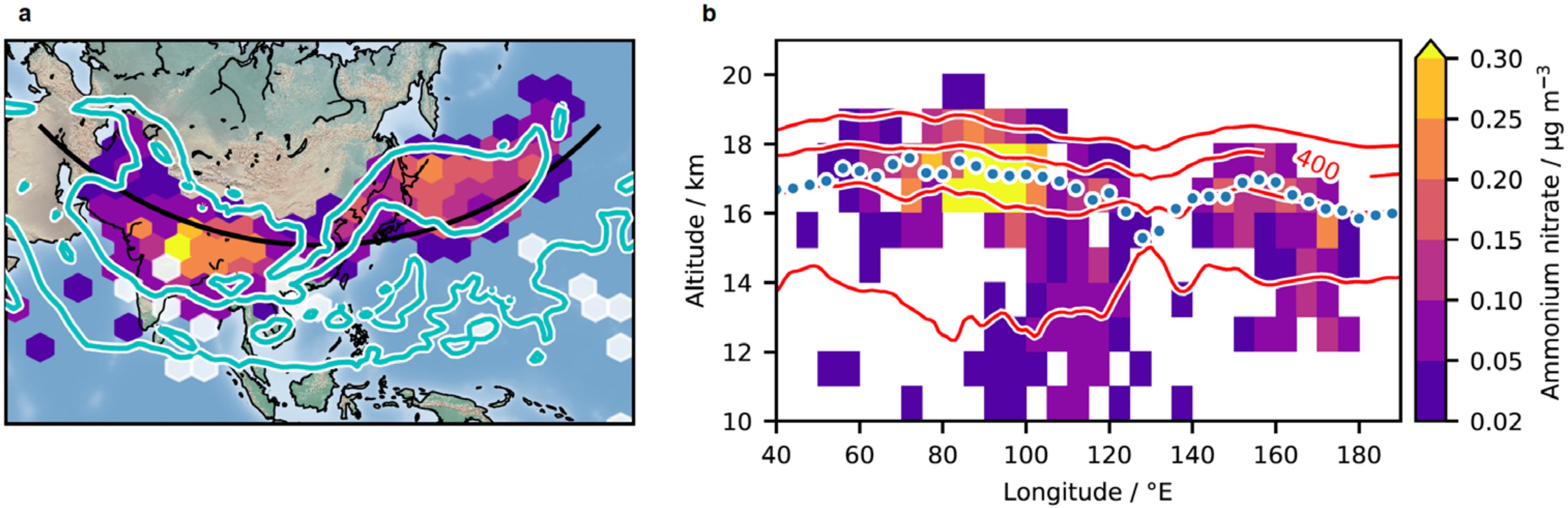
MIPAS/Envisat (2002-2012)

- **IR limb satellite observations allow to derive the vertical and horizontal distribution and temporal evolution of ammonium nitrate and ammonia in the monsoon upper troposphere: 2002-2012**

Höpfner et al., Nat. Geosci, 2019, 10.1038/s41561-019-0385-8, Suppl. Fig. 5

Ammonium nitrate already in 1997

CRISTA
(Aug 1997)



Höpfner et al., Nat. Geosci, 2019, 10.1038/s41561-019-0385-8, Fig. 1

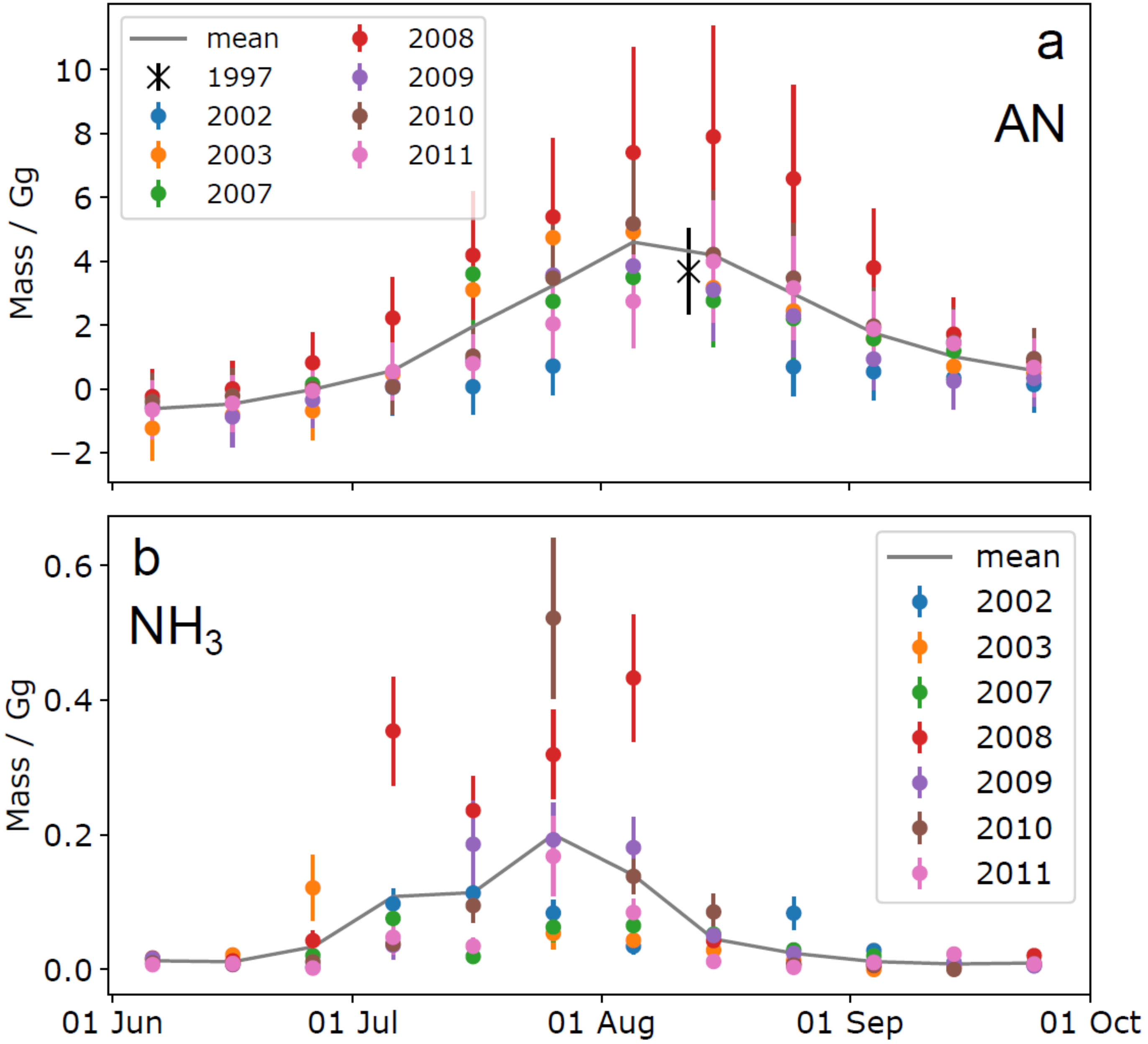
➢ **A layer of ammonium nitrate aerosols already existed during the monsoon in 1997**

MIPAS 2002-2011, CRISTA 1997

Total mass within
10°- 110°E, 20°- 40°N, 13 -17 km

Ammonium nitrate

Ammonia



- **NH_3 in the upper troposphere preceeds ammonium nitrate by 1-2 weeks**

Höpfner et al., Nat. Geosci, 2019, 10.1038/s41561-019-0385-8, Fig. 2

Formation and possible impact of solid ammonium nitrate in the UT

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- Cziczo & Abbatt, 2000, 10.1021/jp9931408: **NH_4NO_3 shows strong inhibition to efflorescence down to 2% RH (298 – 238 K)** "*These findings strongly suggest that, in the absence of heterogeneous nuclei, a **wide variety of inorganic aerosols will exist as liquid solutions** in the atmosphere regardless of relative humidity and temperature conditions*"
- Abbatt et al., 2006, 10.1126/science.1129726: ***Solid Ammonium Sulfate Aerosols as Ice Nuclei****: A Pathway for Cirrus Cloud Formation* (Laboratory and model study)

➢ In contrast to Cziczo&Abbatt: our AIDA experiments show that **solid ammonium nitrate particles form in presence of small impurities (0.6 mol%) of ammonium sulfate at upper tropospheric temperatures**

AIDA experiments on the ice nucleation capability of solid ammonium nitrate particles (Wagner et al., JGR, 2020)

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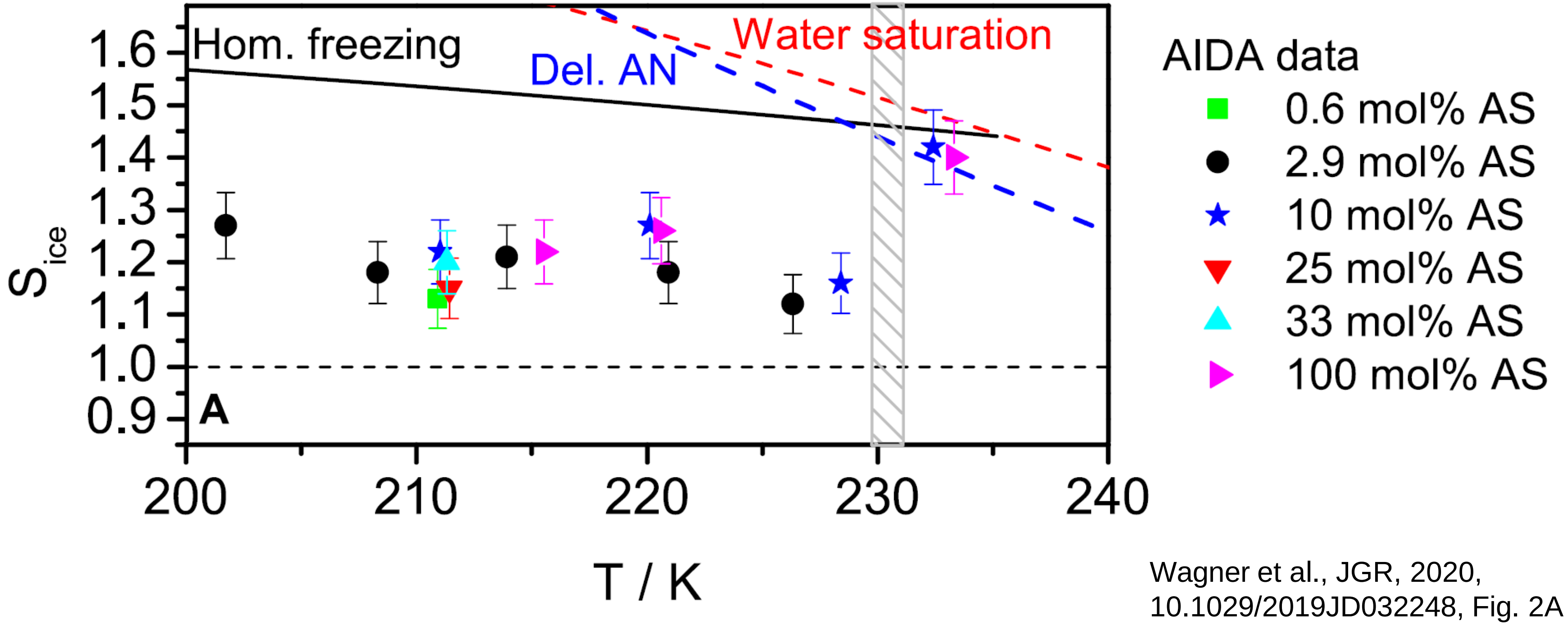

Wagner et al., JGR, 2020,
10.1029/2019JD032248, Fig. 2A

- Crystalline ammonium nitrate particles induce heterogeneous ice nucleation at temperatures below 230 K
- Ice nucleation efficiency of crystalline ammonium nitrate particles is comparable to that of desert dust

Summary

- Observations of **NH_3 concentrations > 1 ppbv in the upper troposphere** during StratoClim in Jul/Aug 2017
- NH_3 source region: Pakistan/NW India, **upward transport by convection** (processes preventing washout are unclear)
- Detection of spectral signal of **solid ammonium nitrate aerosol** particles in limb infrared spectra of CRISTA, MIPAS and GLORIA and in IR absorption spectra in AIDA
- **NH_4NO_3 profiles retrieved from limb-observations** by use of IR mass absorption coefficients as determined in AIDA **fit to in-situ mass spectrometric observations** (see Höpfner et al., Nat. Geosci., 2018)
- **NH_4NO_3 aerosols prevalent in the Asian monsoon anticyclone** following enhanced values of NH_3: evidence that the Asian tropopause aerosol layer (ATAL) consists (at least partly) of ammonium nitrate
- **Crystallization of ammonium nitrate** solution droplets can be induced by the **admixture of very small amounts of ammonium sulfate**
- **Solid NH_4NO_3** particles belong to the **most effective ice nuclei** in the atmosphere (similar to desert dust) and, thus, may **contribute to cirrus cloud formation at low ice saturation** in the region of the ATAL

Acknowledgements

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- Teams developing and operating ERICA at MPI-C and IPA-JGU.
- Members of the Engineering and Infrastructure group at KIT-IMK-AAF.
- Data analysis team of MIPAS at KIT-IMK-ASF.
- CRISTA team at Univ. Wuppertal and Jülich.
- Teams at ULB/LATMOS (Université Libre de Bruxelles/ Laboratoire Atmosphères, Milieux, Observations Spatiales) for provision of the IASI NH3 data.
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Data availability

- CRISTA data: https://datapub.fz-juelich.de/slcs/crista/an/
- MIPAS, GLORIA data for NH_3, AN, trajectory information, AIDA spectra: https://doi.org/10.5445/IR/1000095498
- IASI data on NH3: http://iasi.aeris-data.fr/NH3/
- Low-temperature infrared extinction spectra, temperature- and composition-dependent ice nucleation onsets, and ice nucleation active surface site densities of crystalline AN/AS particles: https://doi.org/10.5445/IR/1000117836