Trace gases and aerosols in the AMA as observed by airborne infrared limb-imaging during StratoClim, Kathmandu, July 2017

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Institute of Meteorology and Climate Research

Two nobel prices 100 years ago

Chemistry

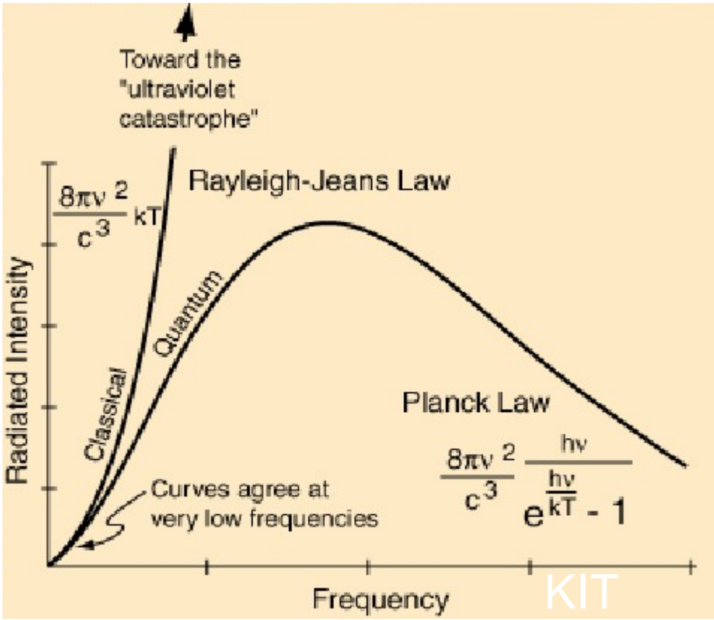
Physics

Fritz Haber

Nobel foundation archive

The Nobel Prize in Chemistry 1918 was received by Fritz Haber in 1919: "for the synthesis of ammonia from its elements."

The Nobel Prize in Physics 1918 was received by Max Planck in 1919: "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta.“

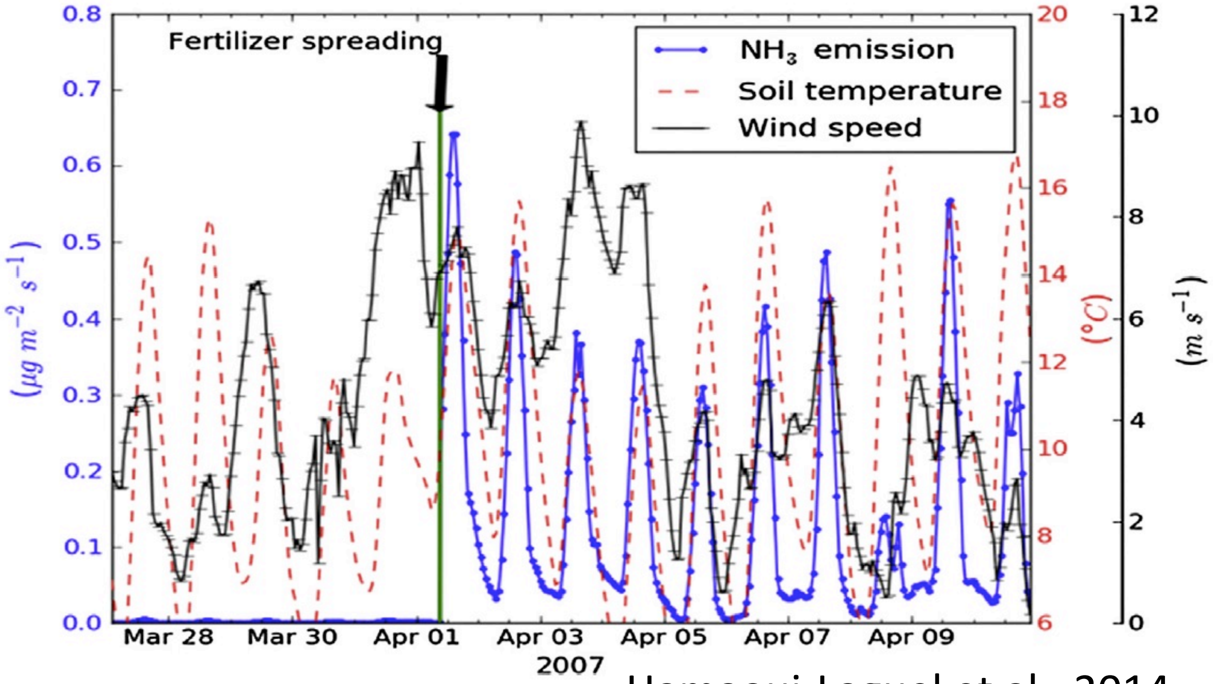


Max Planck

Nobel foundation archive

Significance of ammonia (NH_3)

- Main alkaline species in the atmosphere
- Major source: **agriculture**
- Formation of aerosols by neutralization of acids: **ammonium sulfate** and **ammonium nitrate** depending on the availability of H_2SO_4 and HNO_3
- Important fraction of fine particulate matter
- **Increase of NH_3 emissions in the future**: compensation of aerosol radiative forcing change by reduction of SO_2 emissions
- Important for the **initial nucleation of sulfate aerosols under cold temperatures**



Hamaoui-Laguel et al., 2014

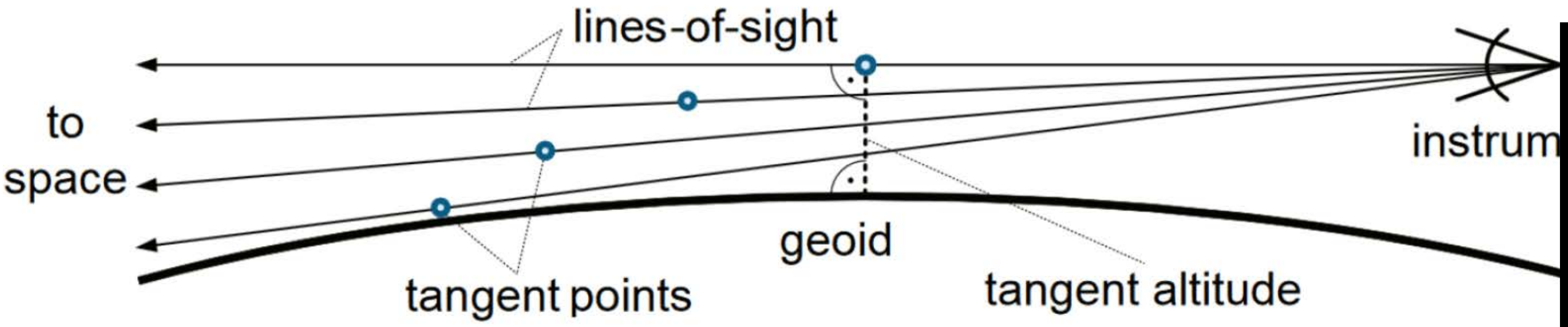
LETTER Kirkby et al., Nature, 2011

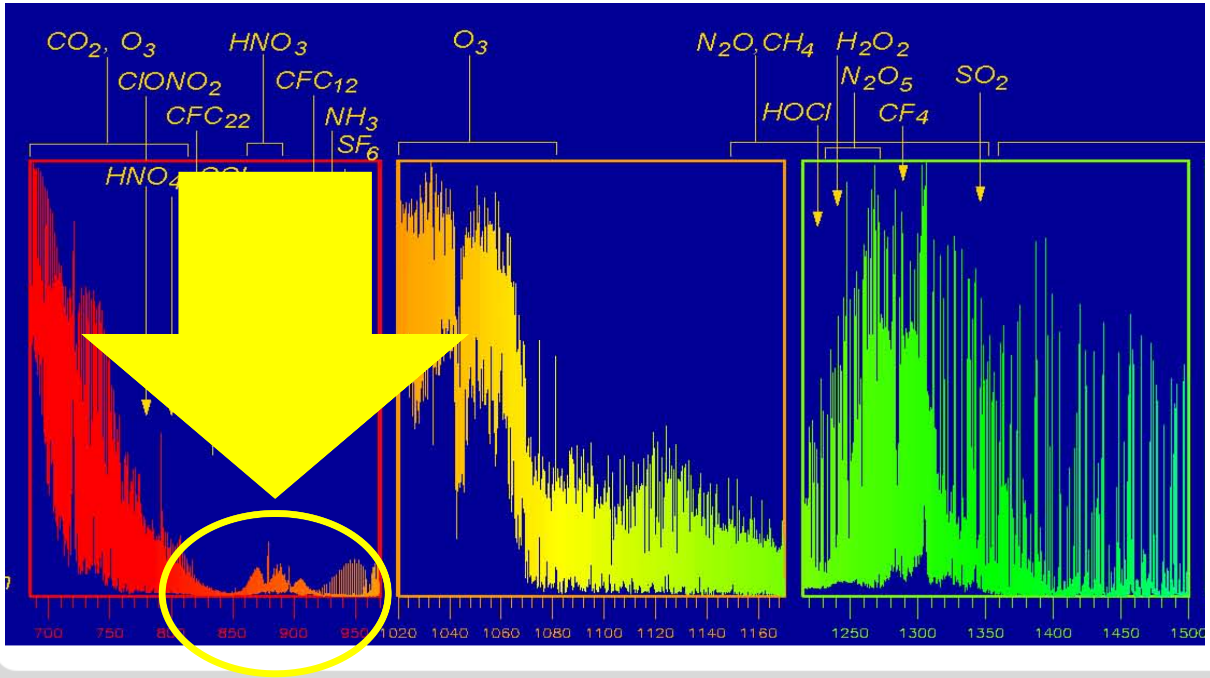
doi:10.1038/nature10343

Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation

But: Difficult to measure in-situ

Infrared limb sounding

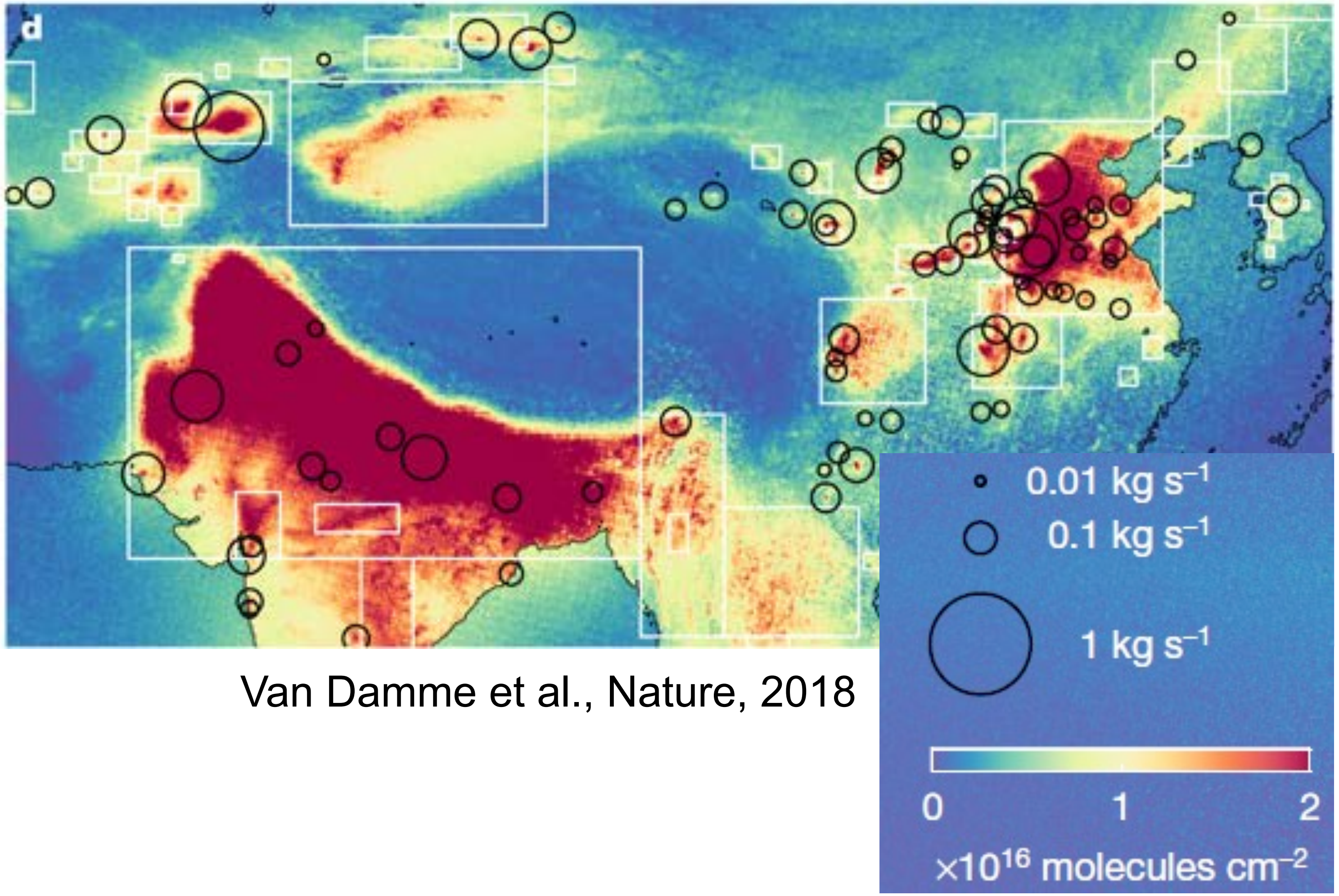




GLORIA@
Geophysica 2017

Observing NH_3

- Ground-based in-situ
- Airborne in-situ up to ~5 km
- Balloon-borne in-situ (no detection above 8 km)
- Ground-based FTIR (columns)
- **Satellite: IR nadir sounding (e.g. IASI)**
- **For the first time detected in the upper troposphere by IR limb sounding (MIPAS)**

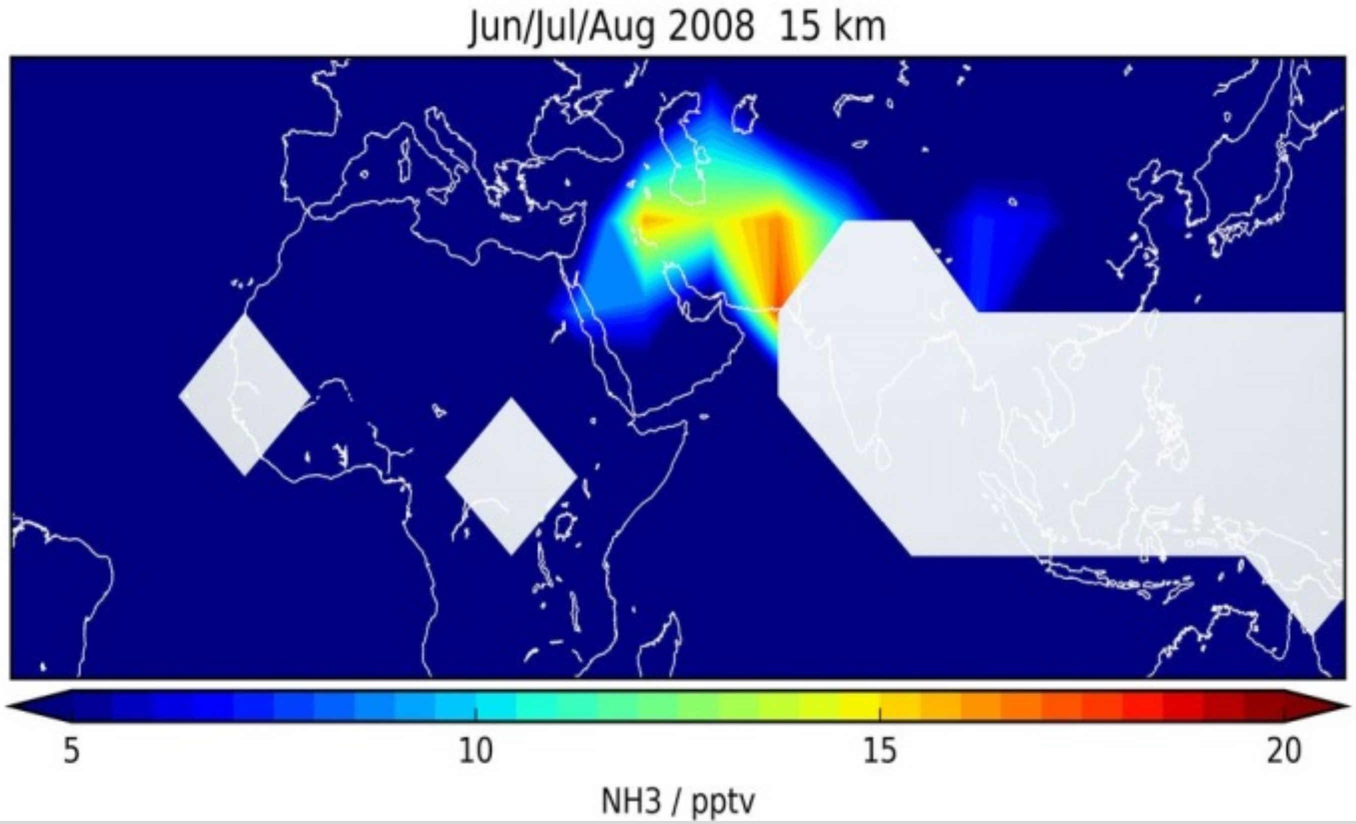


Van Damme et al., Nature, 2018

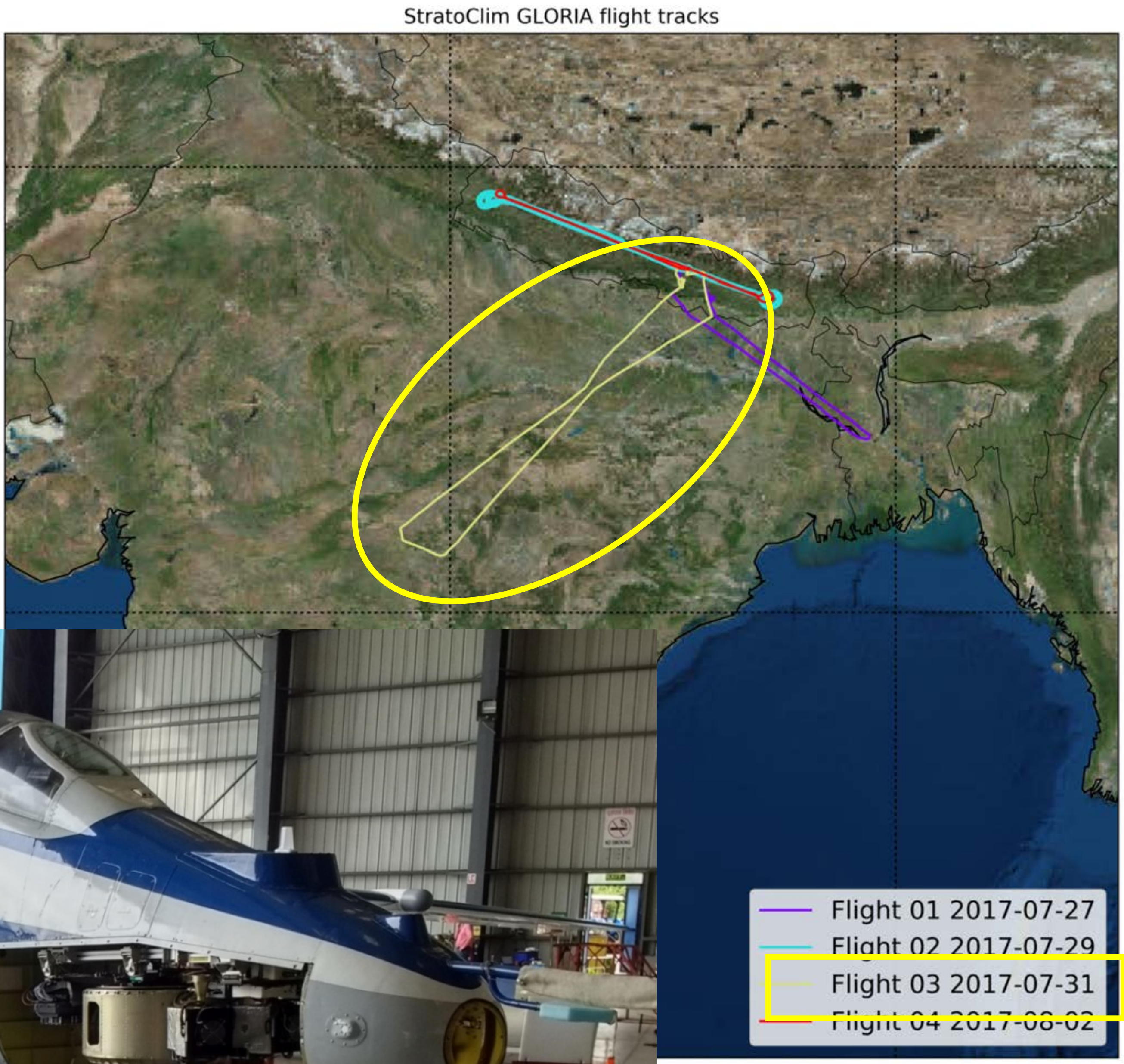
MIPAS-Envisat:
NH_3 in the Upper Troposphere

Karlsruhe Institute of Technology

- Evidence for the presence of ammonia in the upper troposphere (Höpfner et al., ACP, 2016)
- Enhanced 3-monthly mean values of up to ~30 pptv within the Asian monsoon upper troposphere

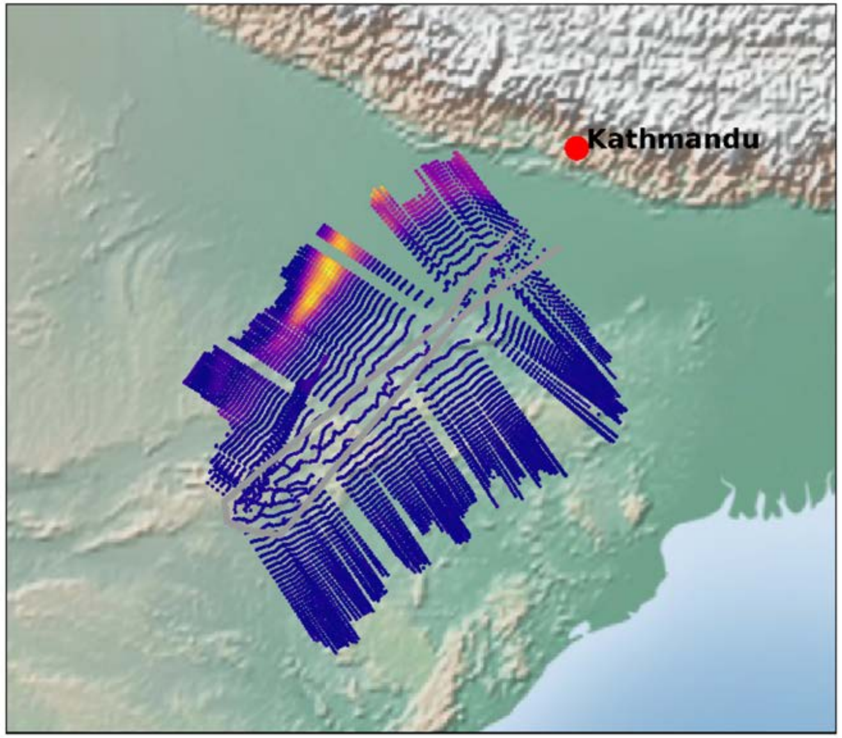


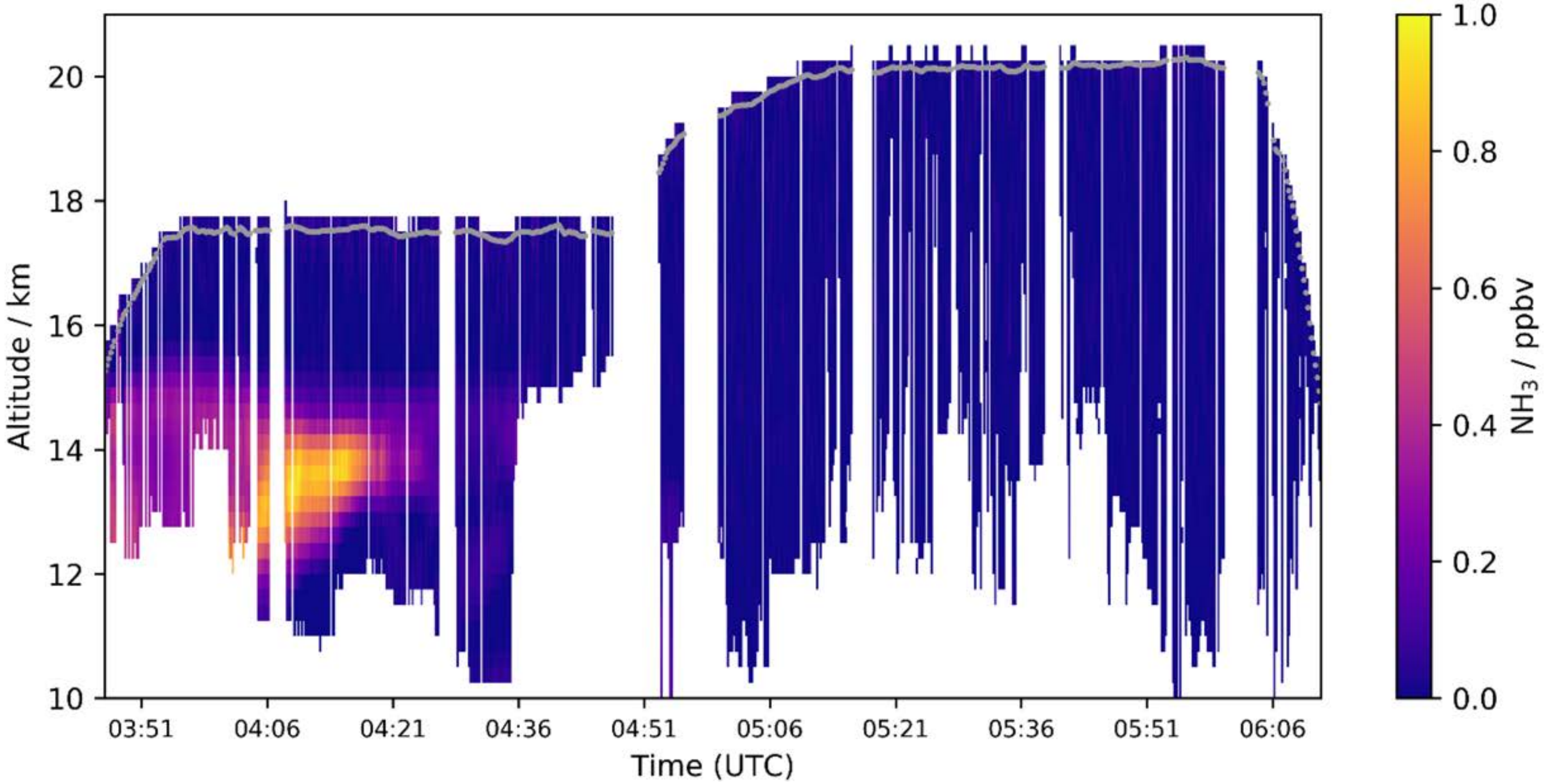
Flights with GLORIA

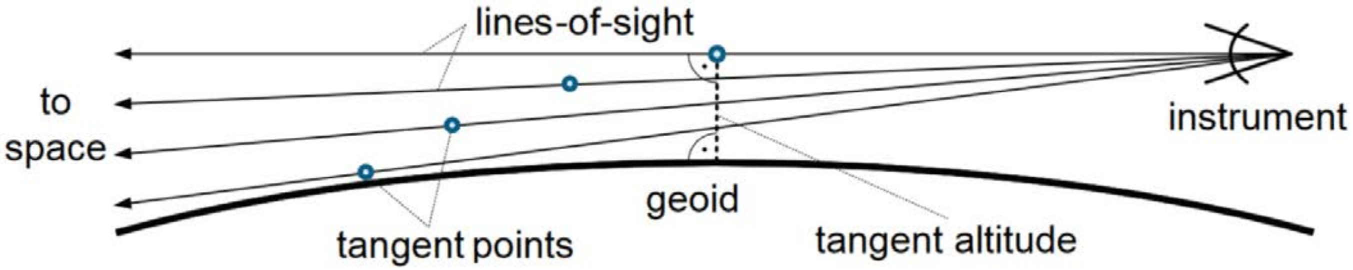


StratoClim flight 31 Jul 2017

NH_3



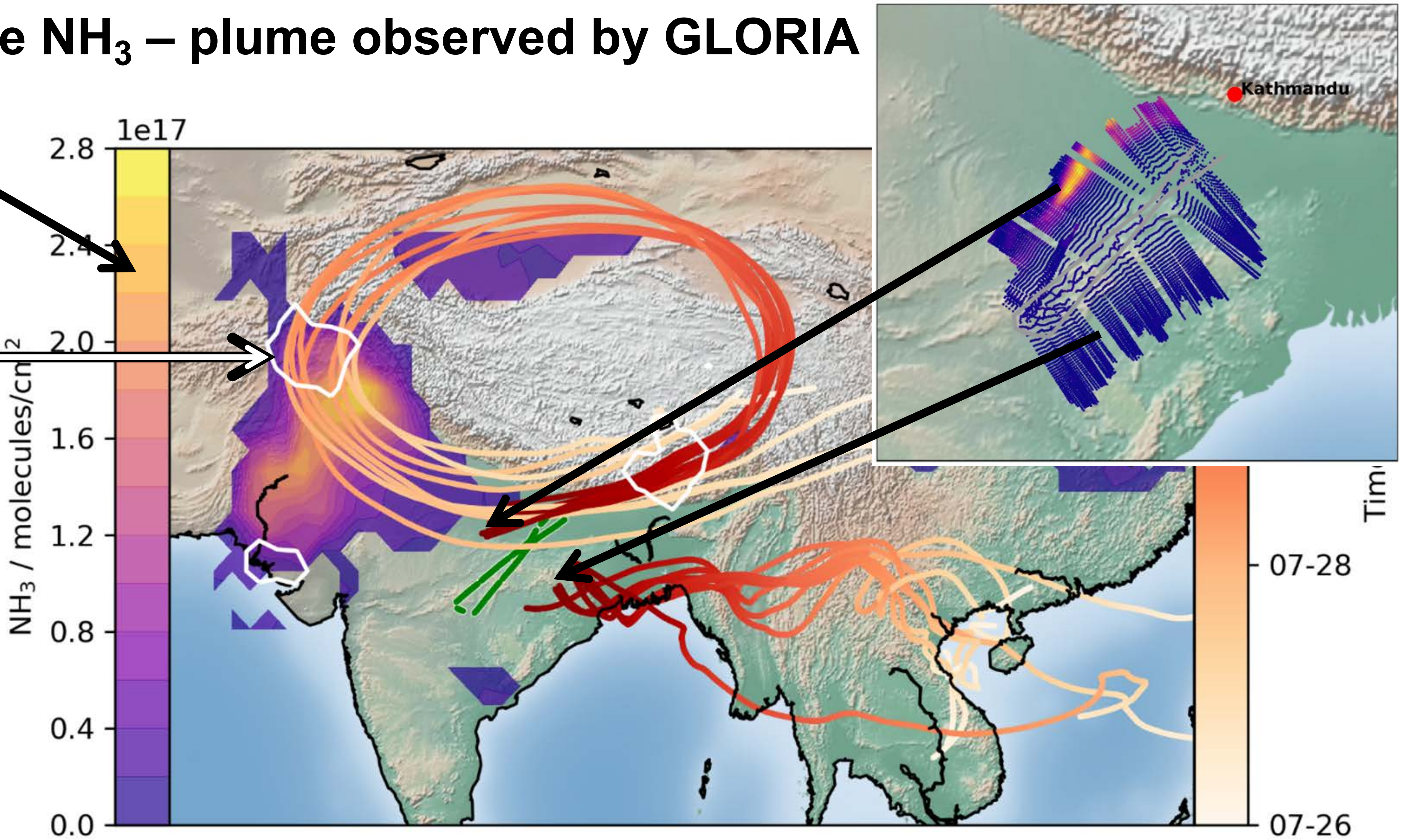




Origin of the NH_3 – plume observed by GLORIA

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

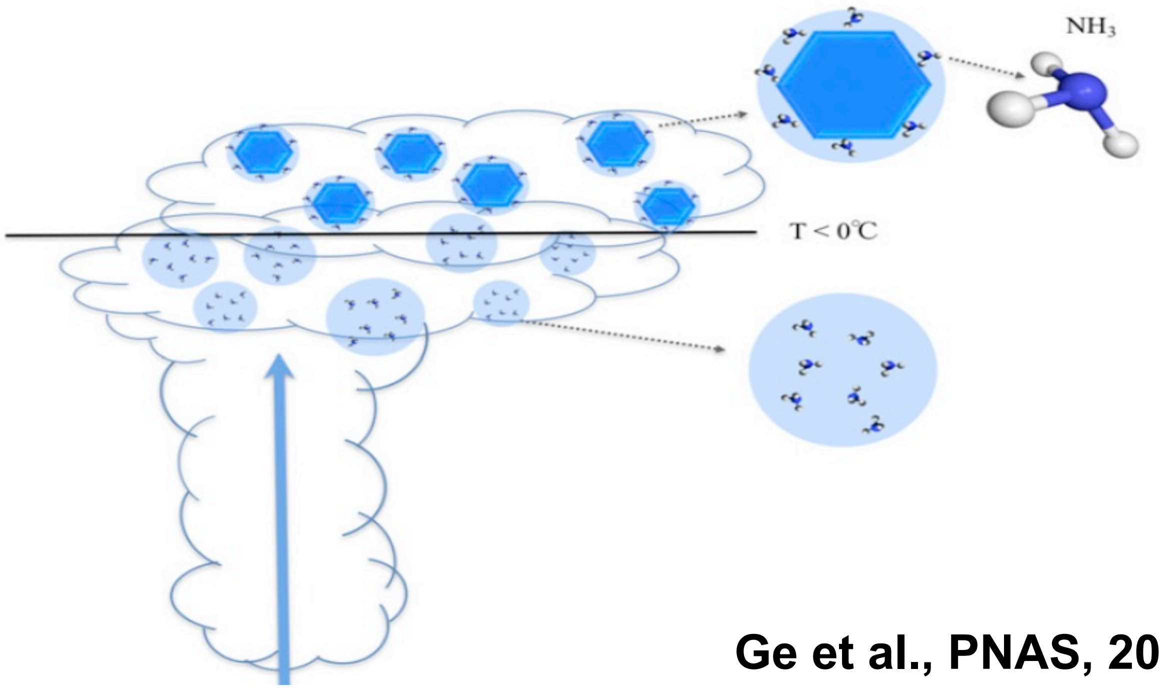
Why is NH_3 not washed out during convection?

Karlsruhe Institute of Technology

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 NH_3 observations
- "We show that the NH_3 dissolved in liquid cloud droplets is prone to being released into the UTLS upon freezing during deep convection."



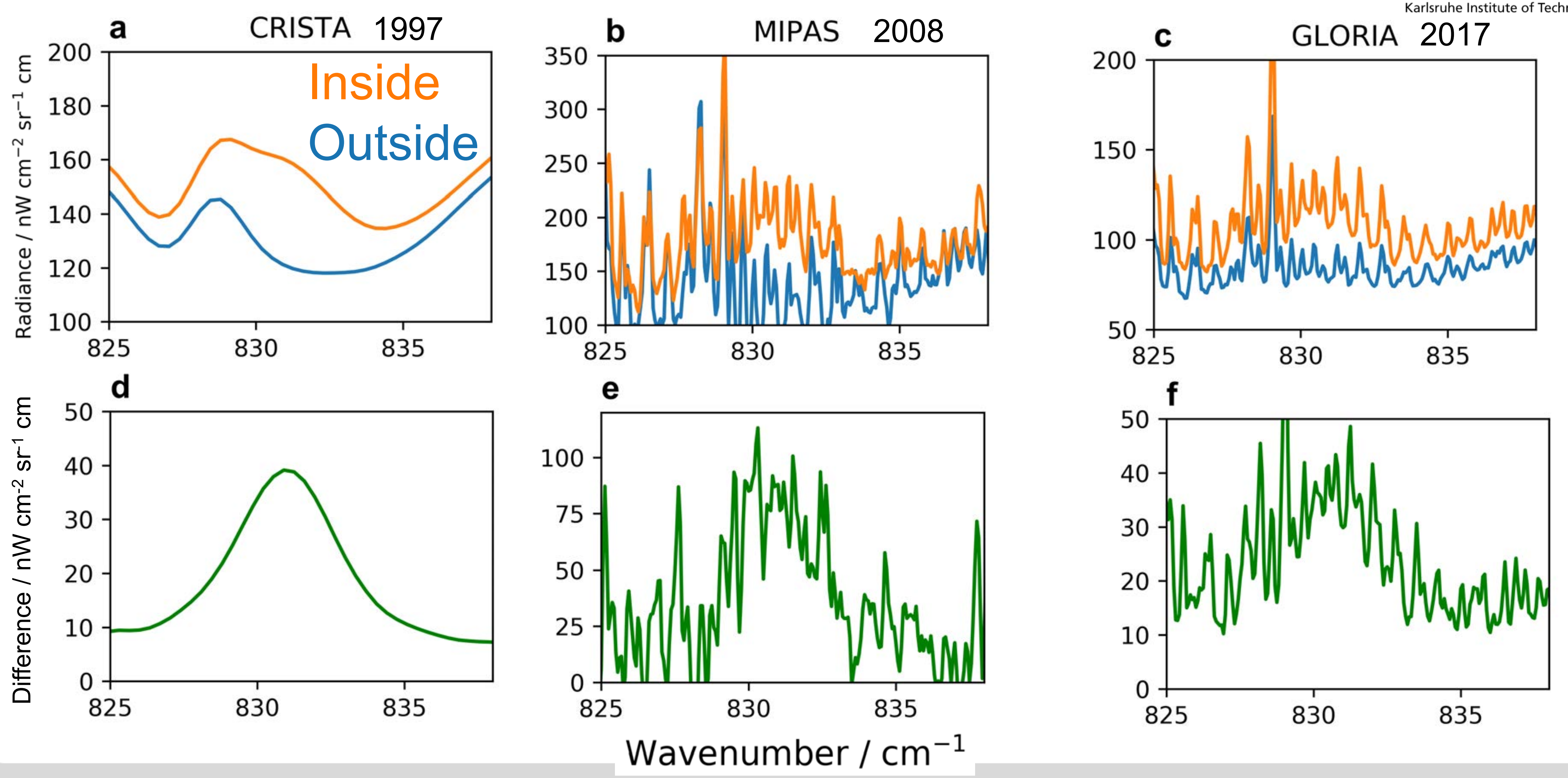
Ge et al., PNAS, 2018

?

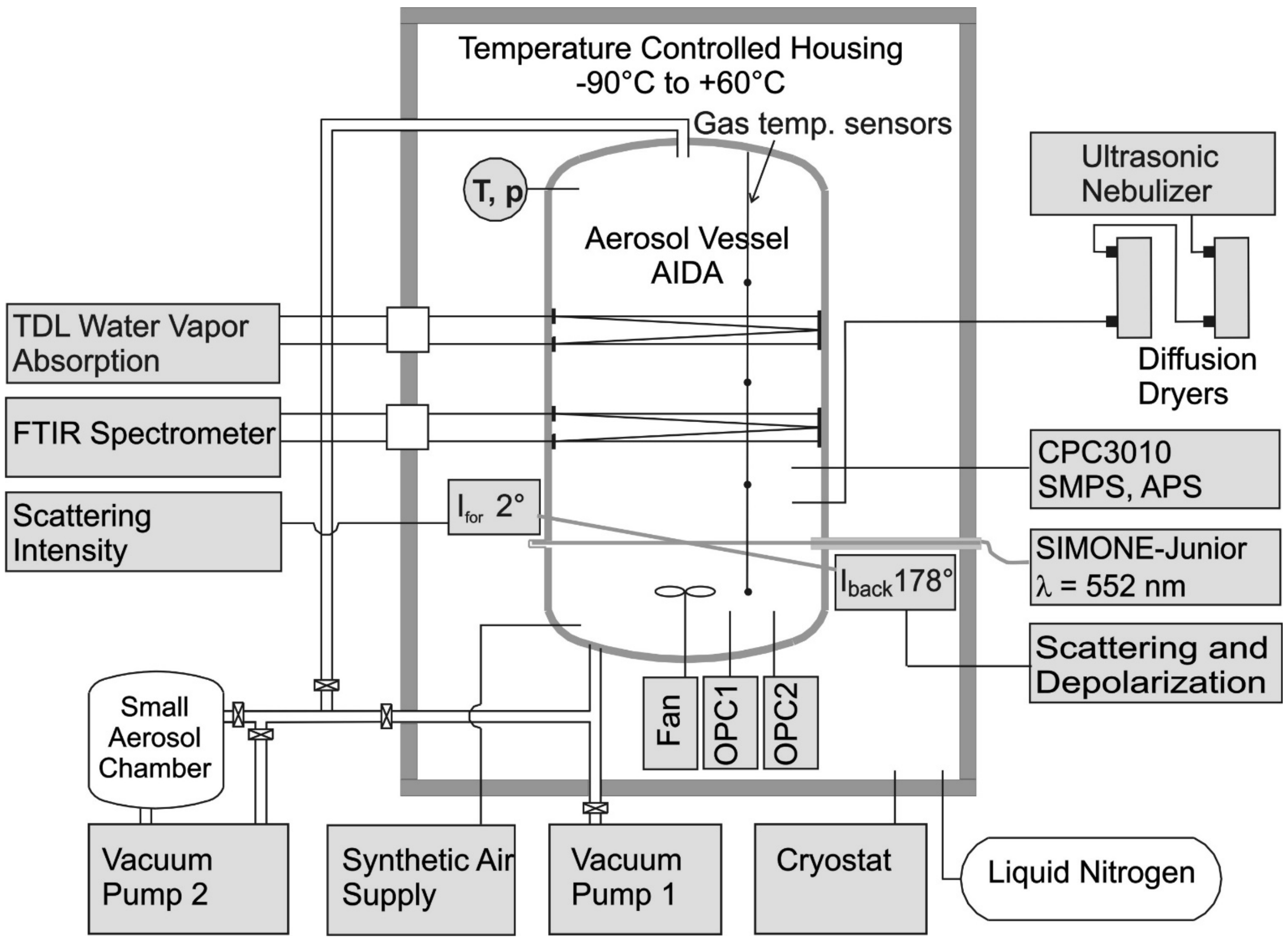
- ph – dependence of NH_3 solubility in liquid water: „Convective clouds are hardly acidic so that NH_3 is only partlhy dissolved and removed by precipitation“

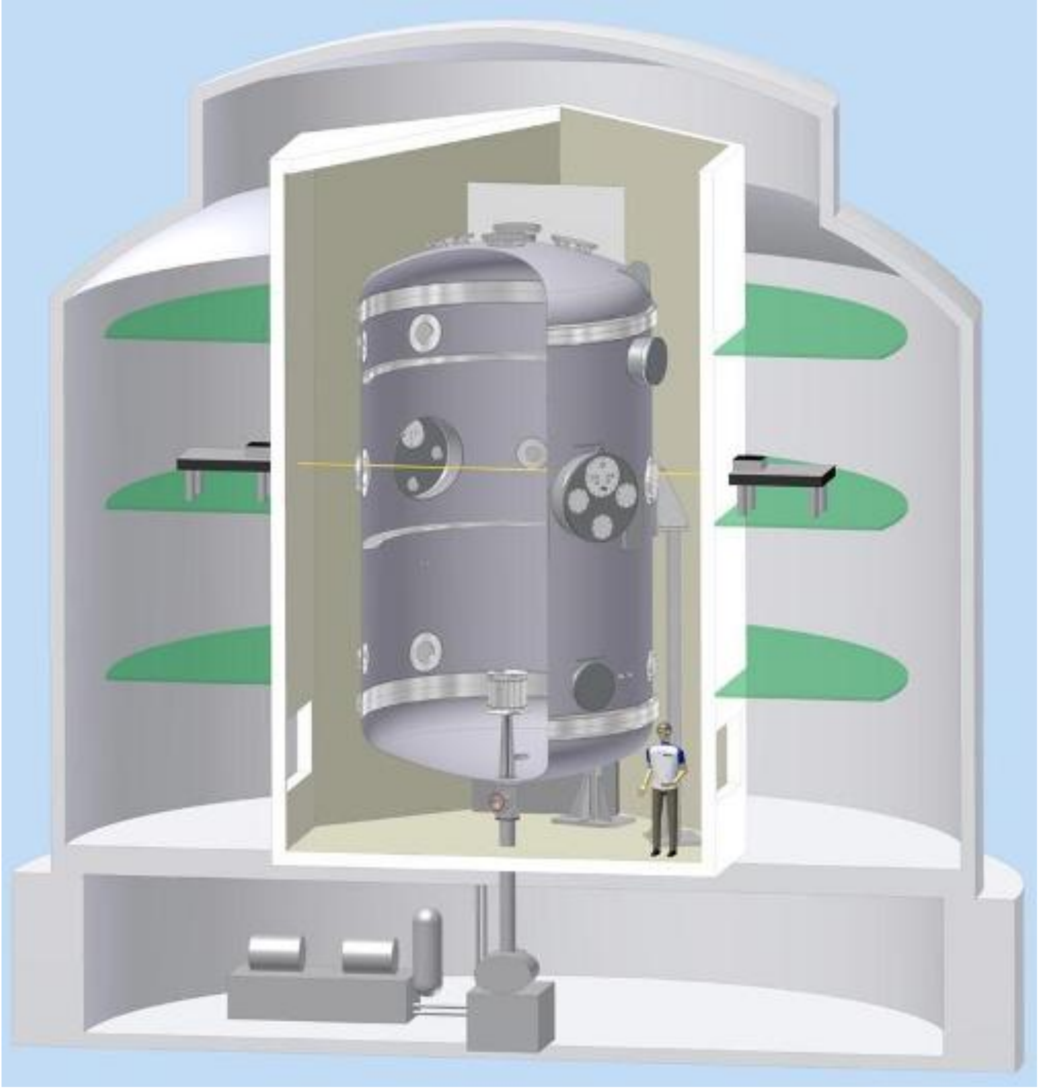
Metzger et al., JGR, 2002

A peak in infrared spectra inside the monsoon upper troposphere at 831 cm^{-1}



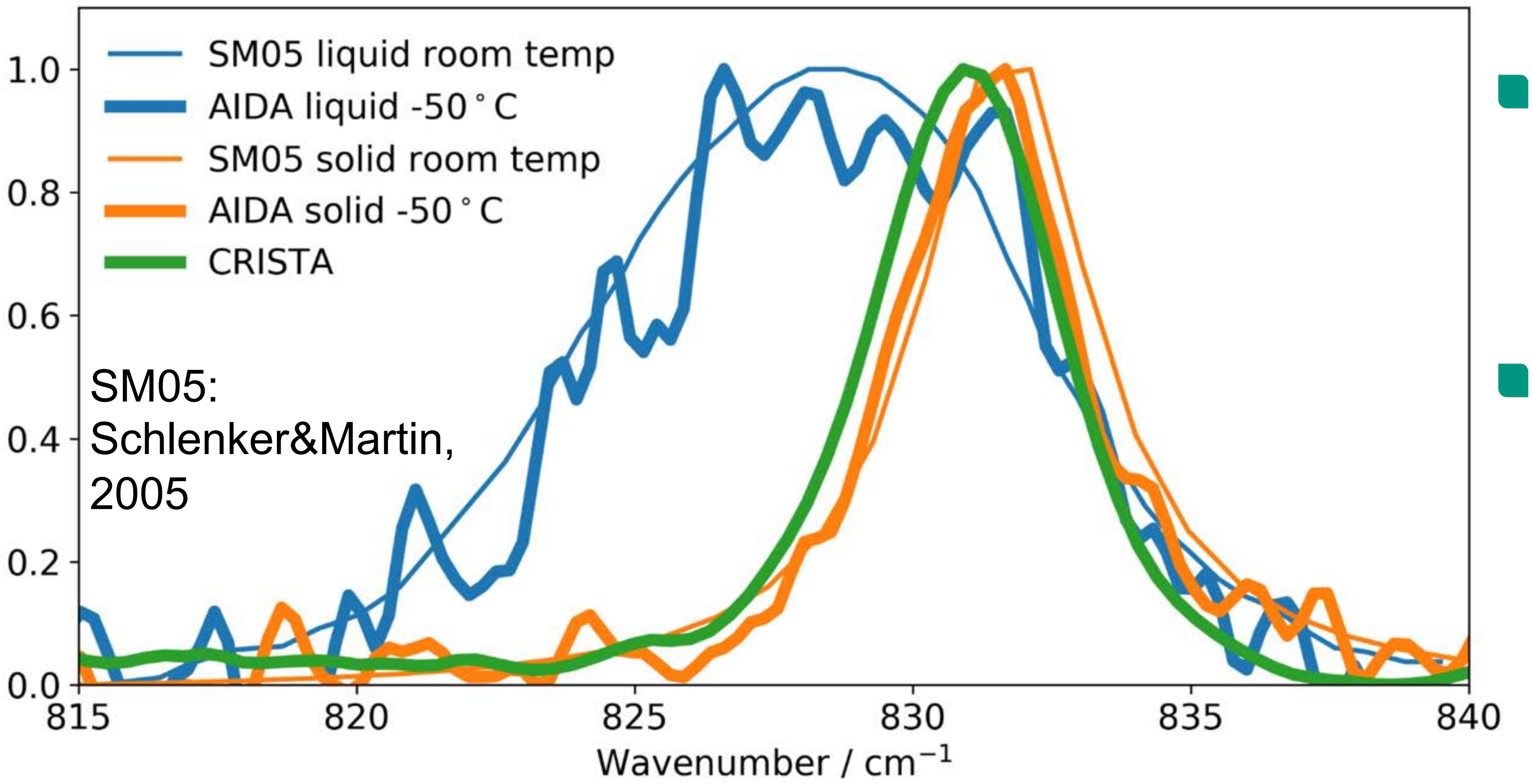
The AIDA aerosol and cloud chamber





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

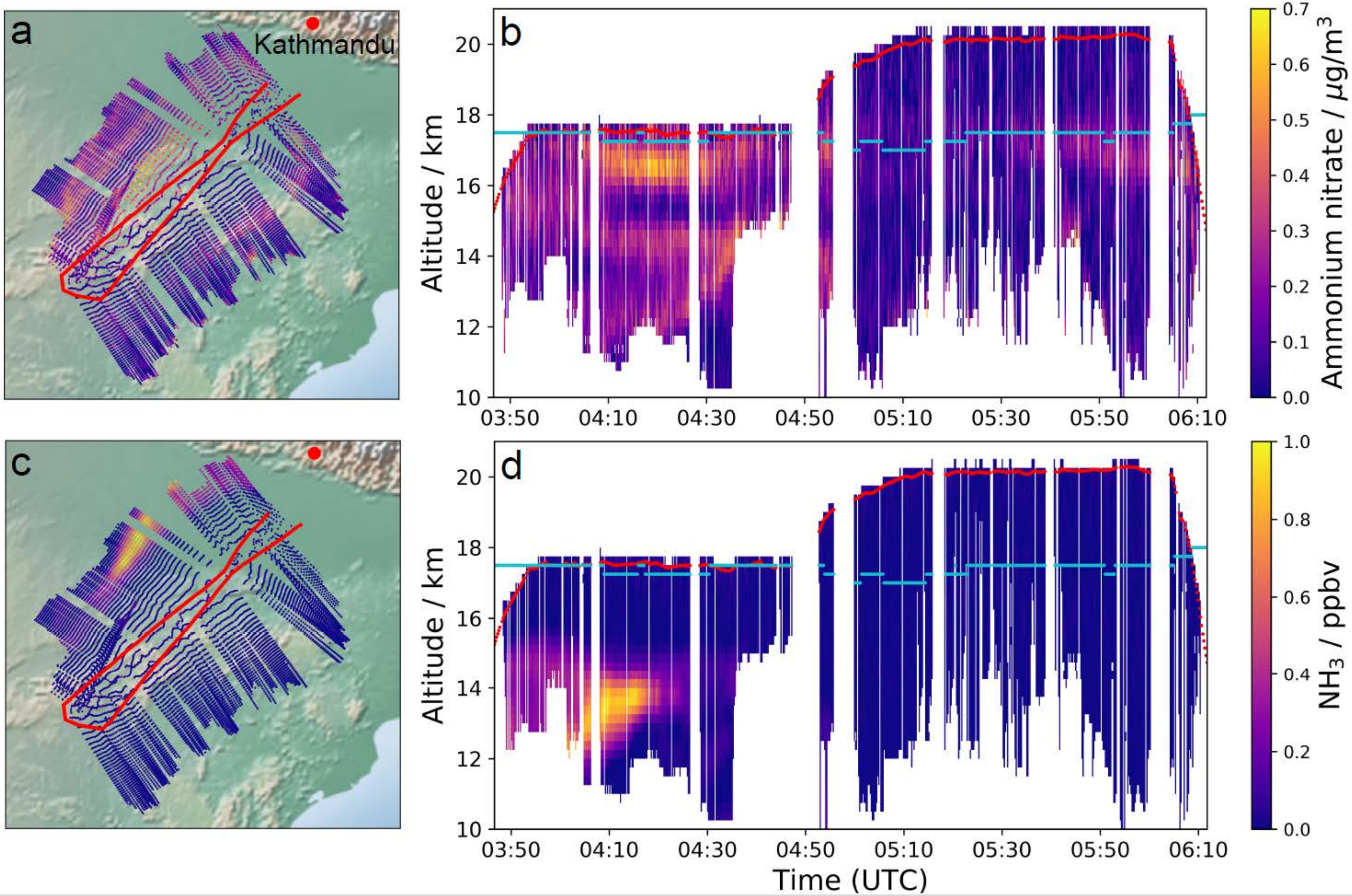
Karlsruhe Institute of Technology



- Observed peak fits to the signature of **solid ammonium nitrate**
- **Liquid ammonium nitrate** has a much broader peak and **does not fit the observations**

→ **AIDA observations allow to derive ammonium nitrate mass concentration profiles from the infrared limb observations**

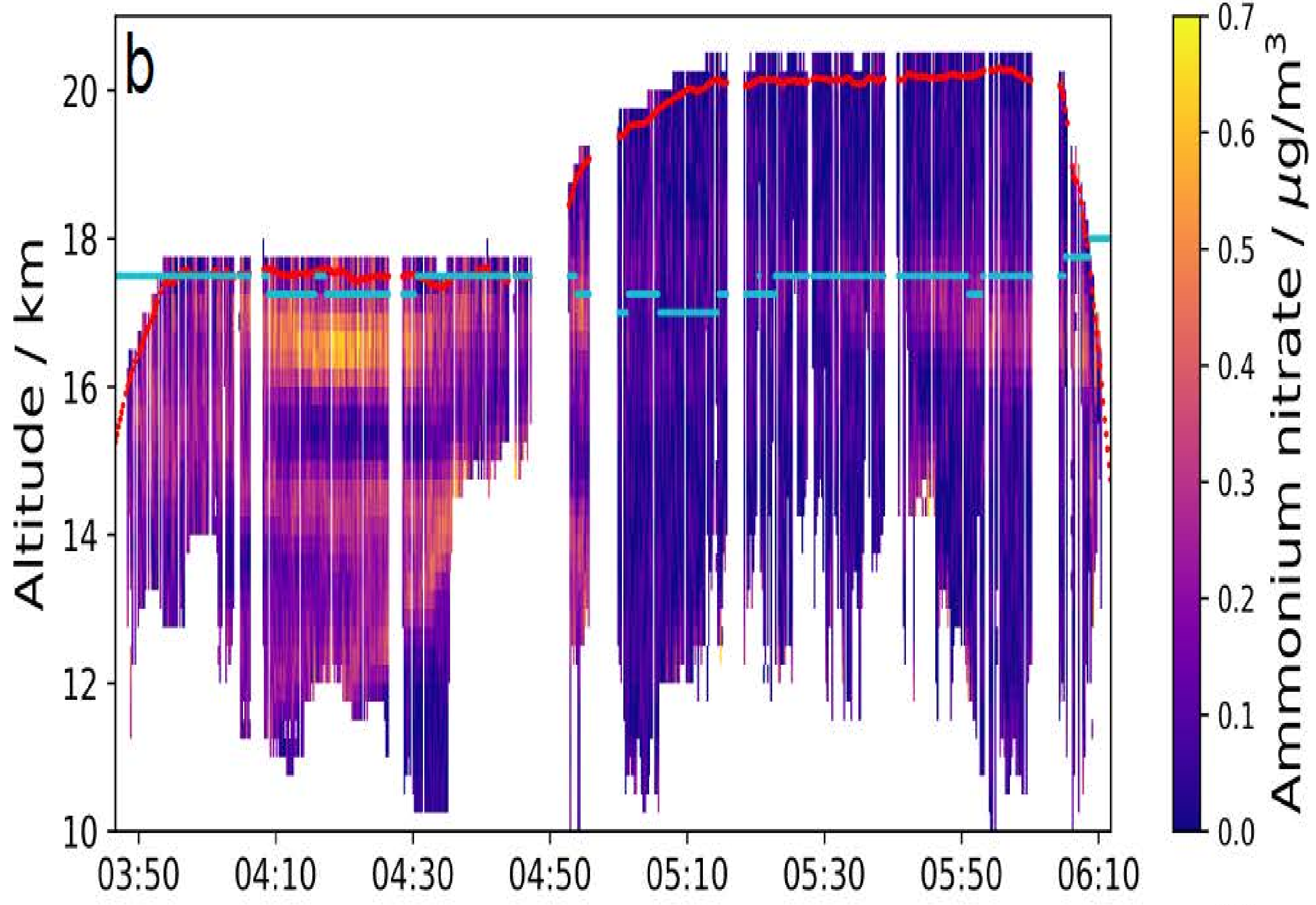
StratoClim flight 31 Jul 2017

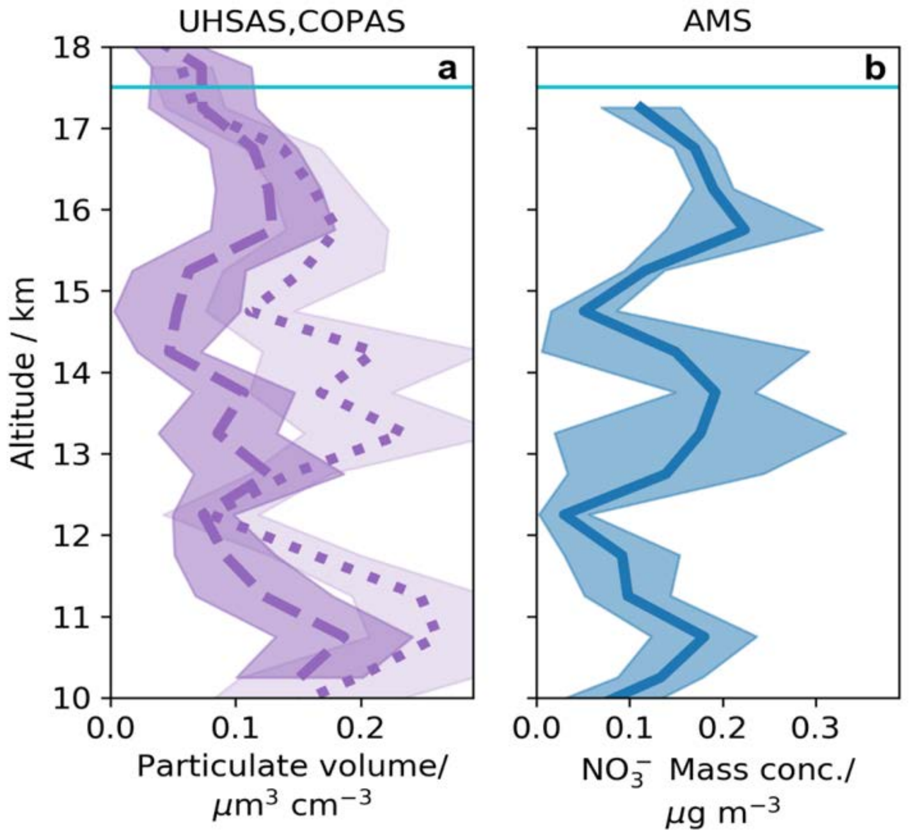


NH_4NO_3 aerosol mass density

NH_3 trace gas mixing ratio

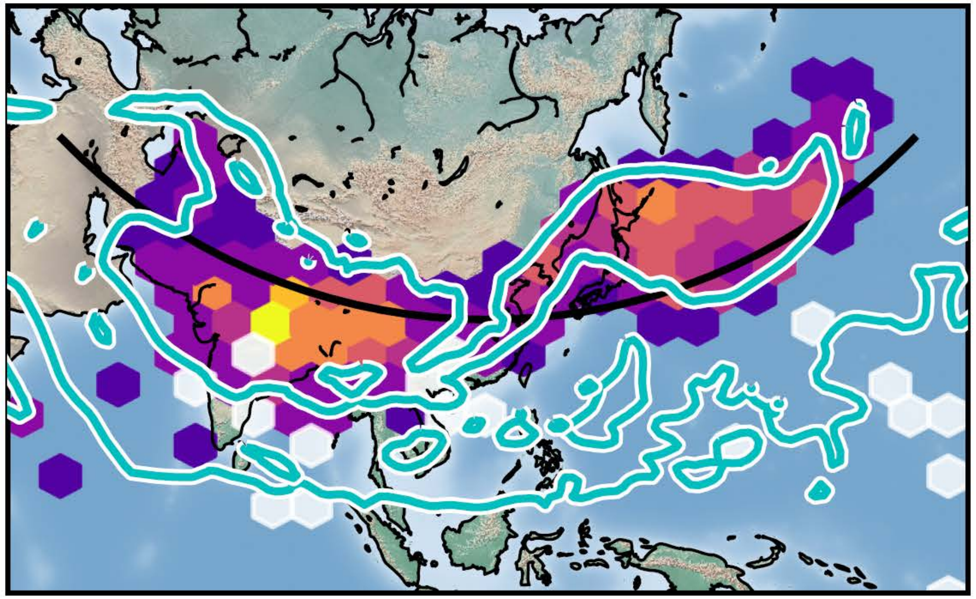
StratoClim flight 31 Jul 2017: comparison with in-situ aerosol measurements of Univ./MPI Mainz



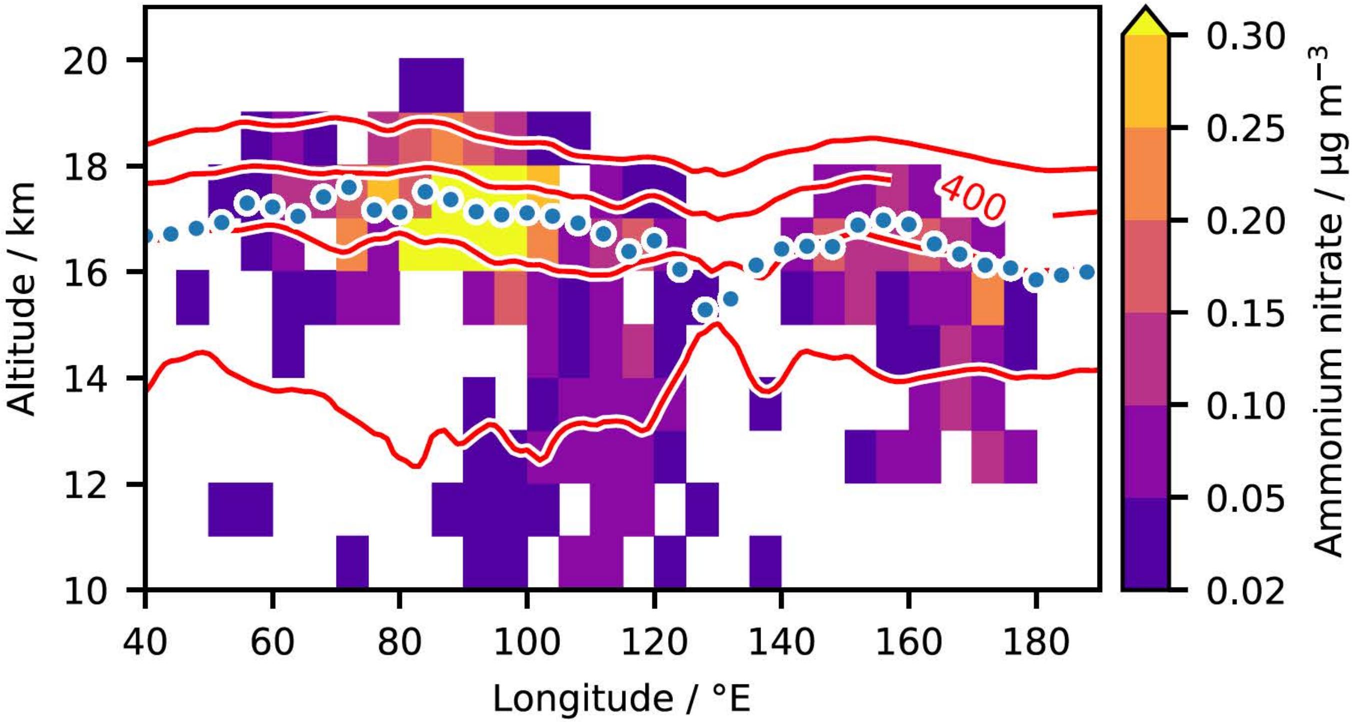


CRISTA ammonium nitrate
August 1997

a

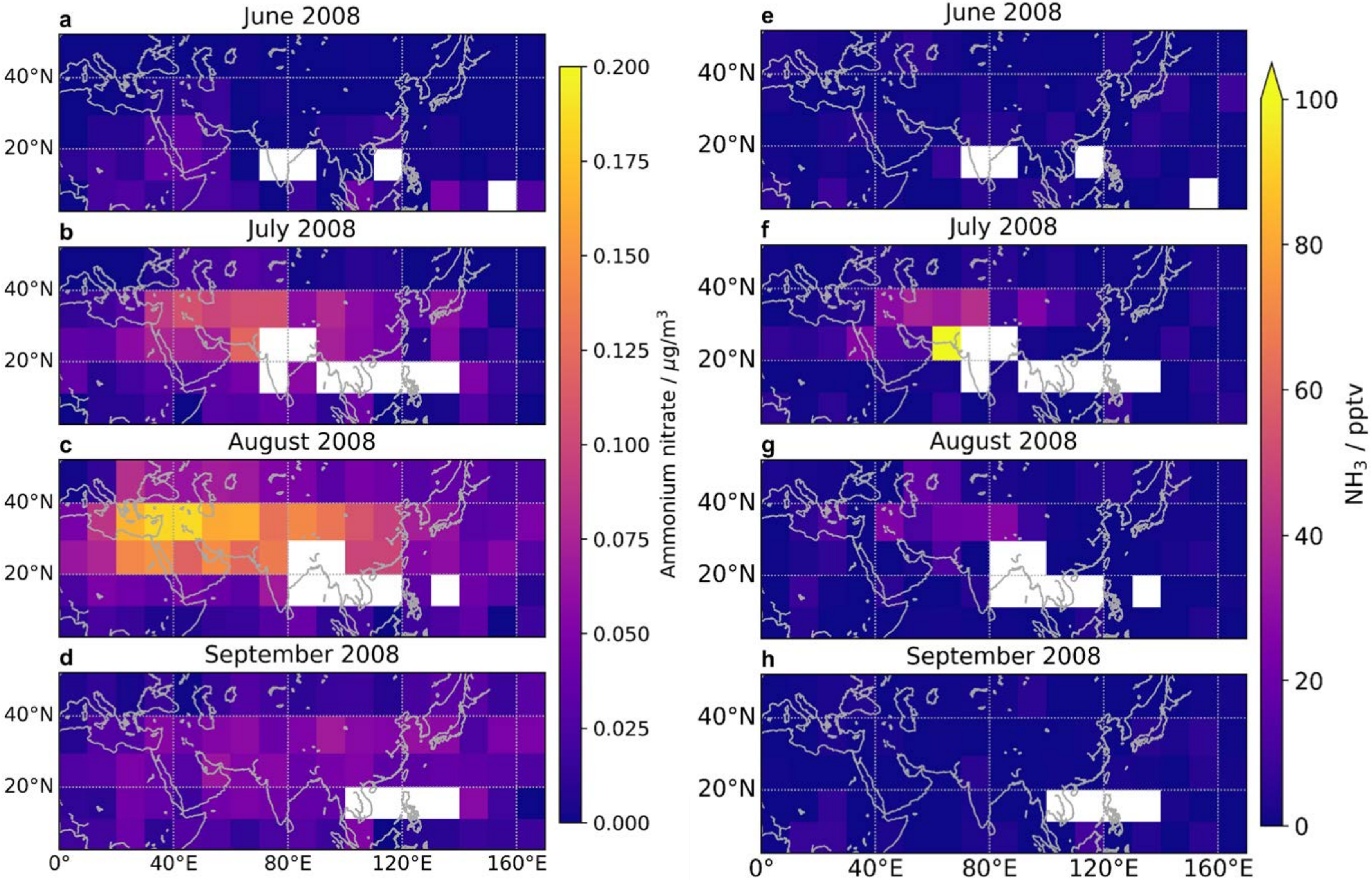


b



NH_4NO_3 aerosol mass density

NH_3 trace gas mixing ratio



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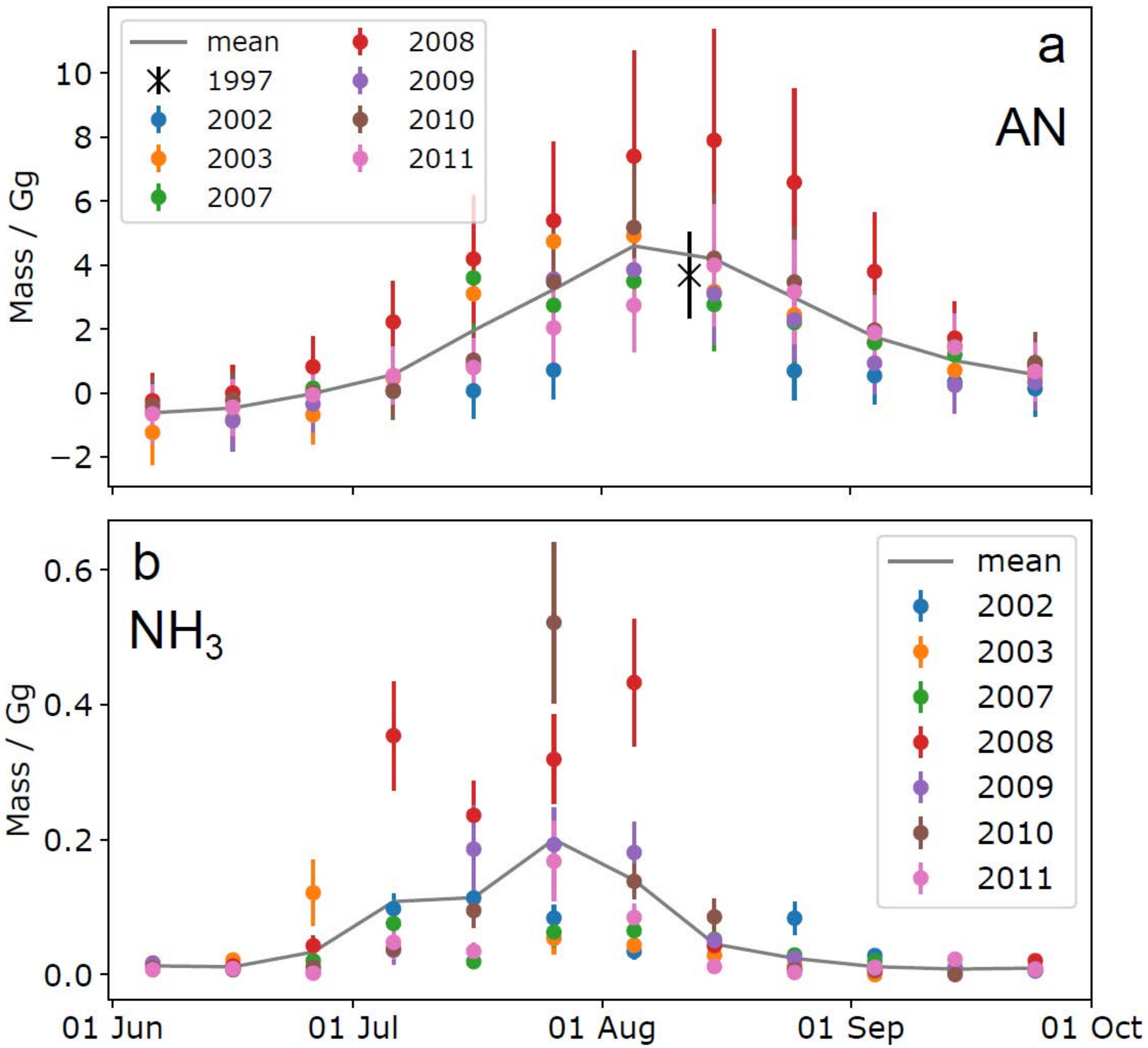
MIPAS 2008

MIPAS 2002-2011

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

Ammonium nitrate

Ammonia



Formation and possible impact of solid ammonium nitrate in the UT

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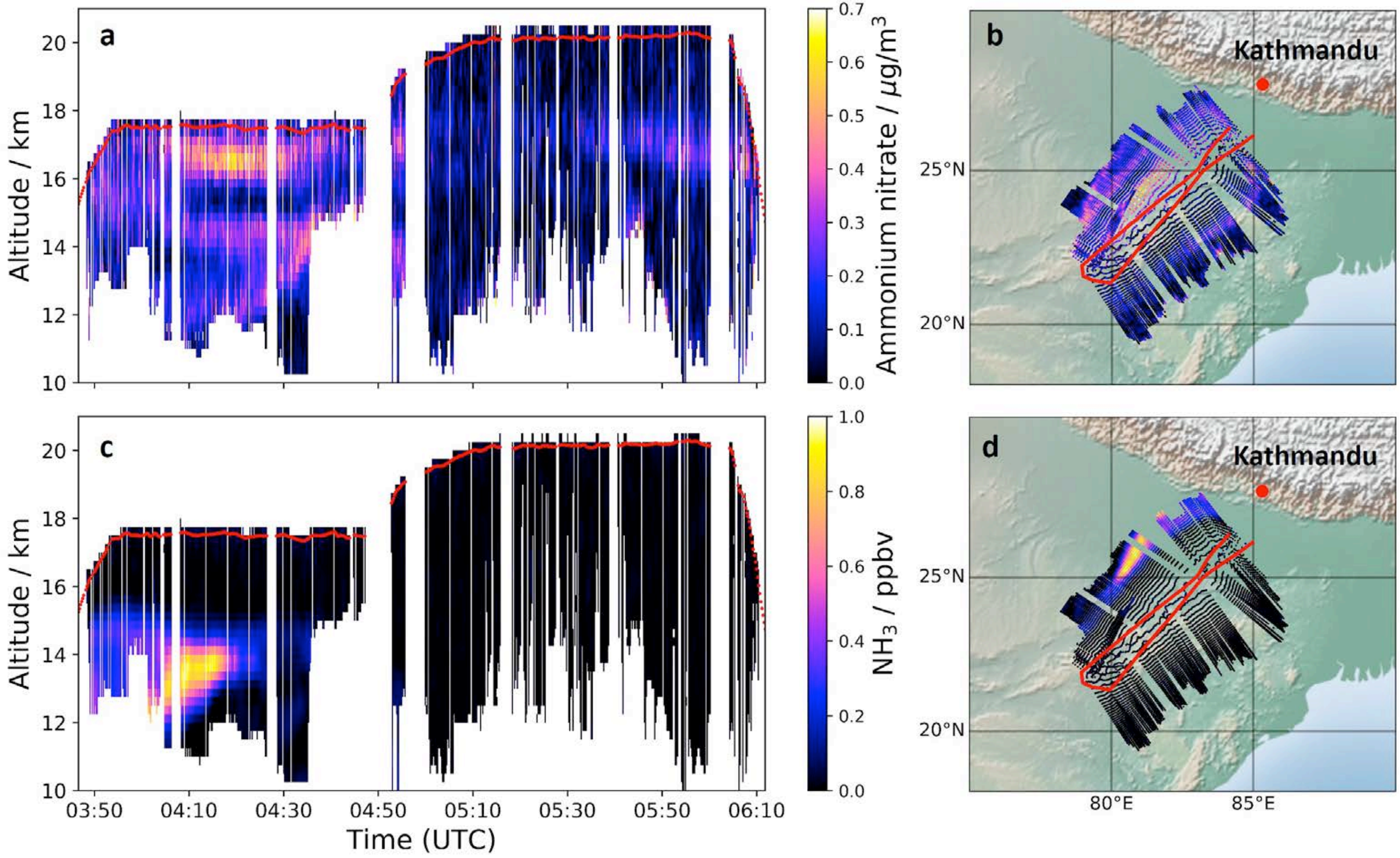
- Cziczo & Abbatt, 2000: **NH_4NO_3 shows strong inhibition to efflorescence down to 2% RH (298 – 238 K)** "*These findings strongly suggest that, in the absence of heterogeneous nuclei, a **wide variety of inorganic aerosols will exist as liquid solutions** in the atmosphere regardless of relative humidity and temperature conditions*"
- Abbatt et al., Science, 2006: "***Solid Ammonium Sulfate Aerosols as Ice Nuclei**: A Pathway for Cirrus Cloud Formation*" (Laboratory and model study)
- Our AIDA experiments: **solid NH_4NO_3 (223 K) only forms in presence of small impurities (3 mol%) of ammonium sulfate**

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**
- 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**
- **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 (partly) of ammonium nitrate
- **Solid NH_4NO_3 particle formation** in AIDA appears only in the presence of **impurities of $(NH_4)_2SO_4$** - these may act as a **good ice nuclei**

StratoClim flight 31 Jul 2017



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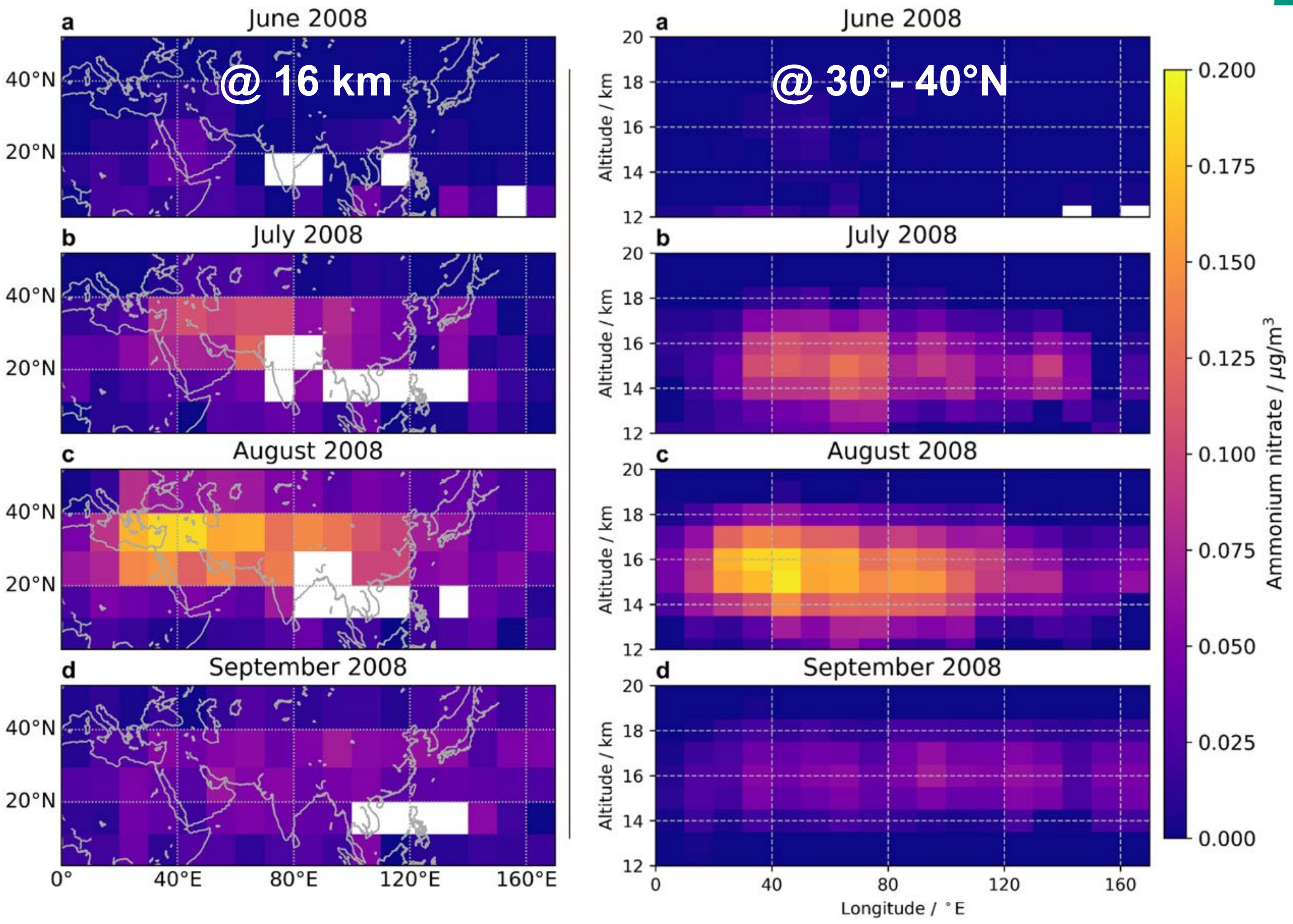
NH_4NO_3 aerosol mass density

NH_3 trace gas mixing ratio

MIPAS 2008: ammonium nitrate



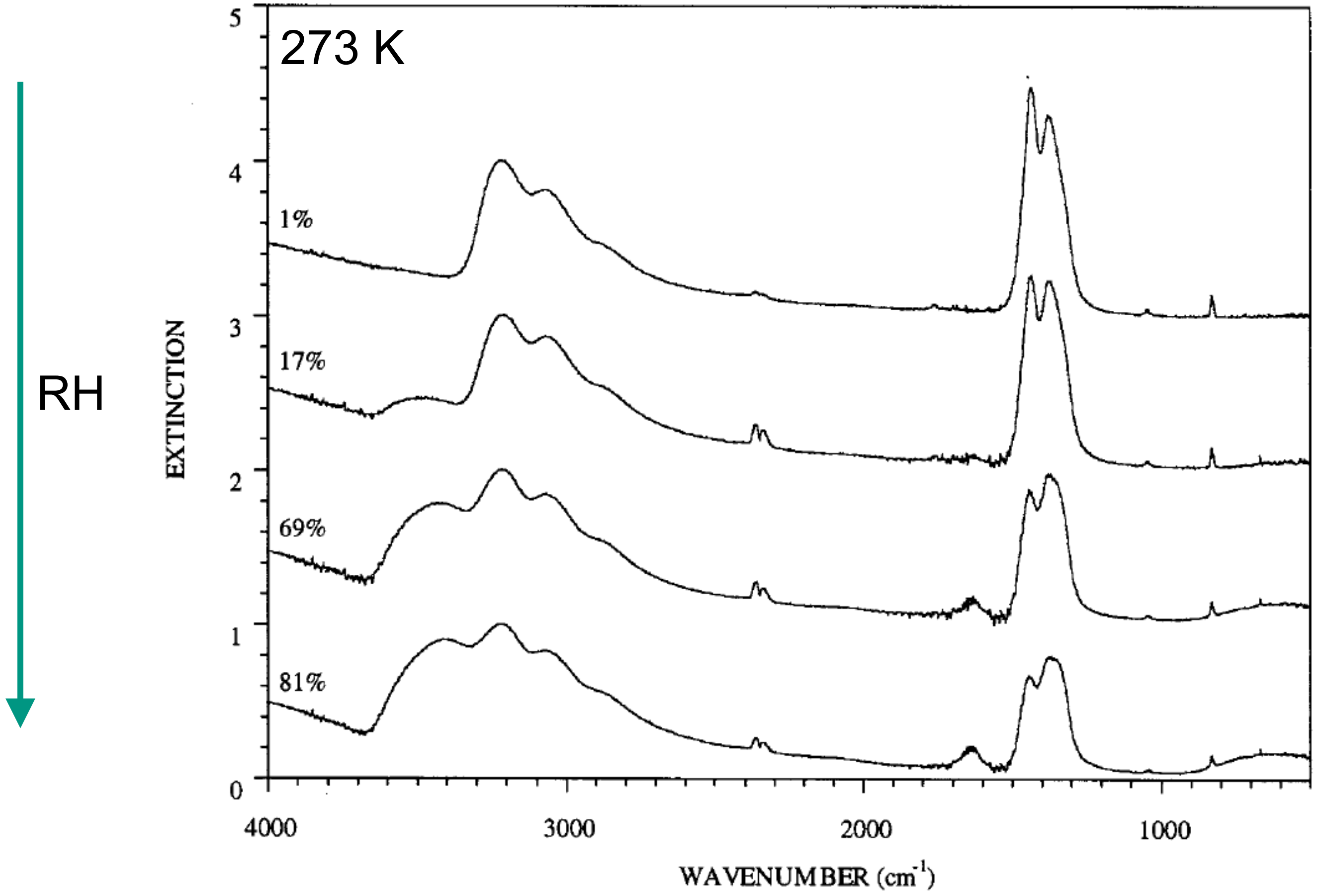
Infrared spectroscopy of ammonium nitrate

The $\nu_2(NO_3^-)$ band of NH_4NO_3 has been assigned in laboratory spectra to wavenumbers around 831 cm^{-1}:

- Théorêt and Sandorfy (1964): 830 cm^{-1} (phase IV)
- Fernandes et al. (1979): 833 cm^{-1} (phase V), 831 cm^{-1} (phase IV)
- Allen et al., 1994: 825-835 cm^{-1}
- Koch et al. (1996): 832 cm^{-1} (phase V), 830 cm^{-1} (phase IV)
- Schlenker and Martin (2005): 831 cm^{-1}

Literature overview

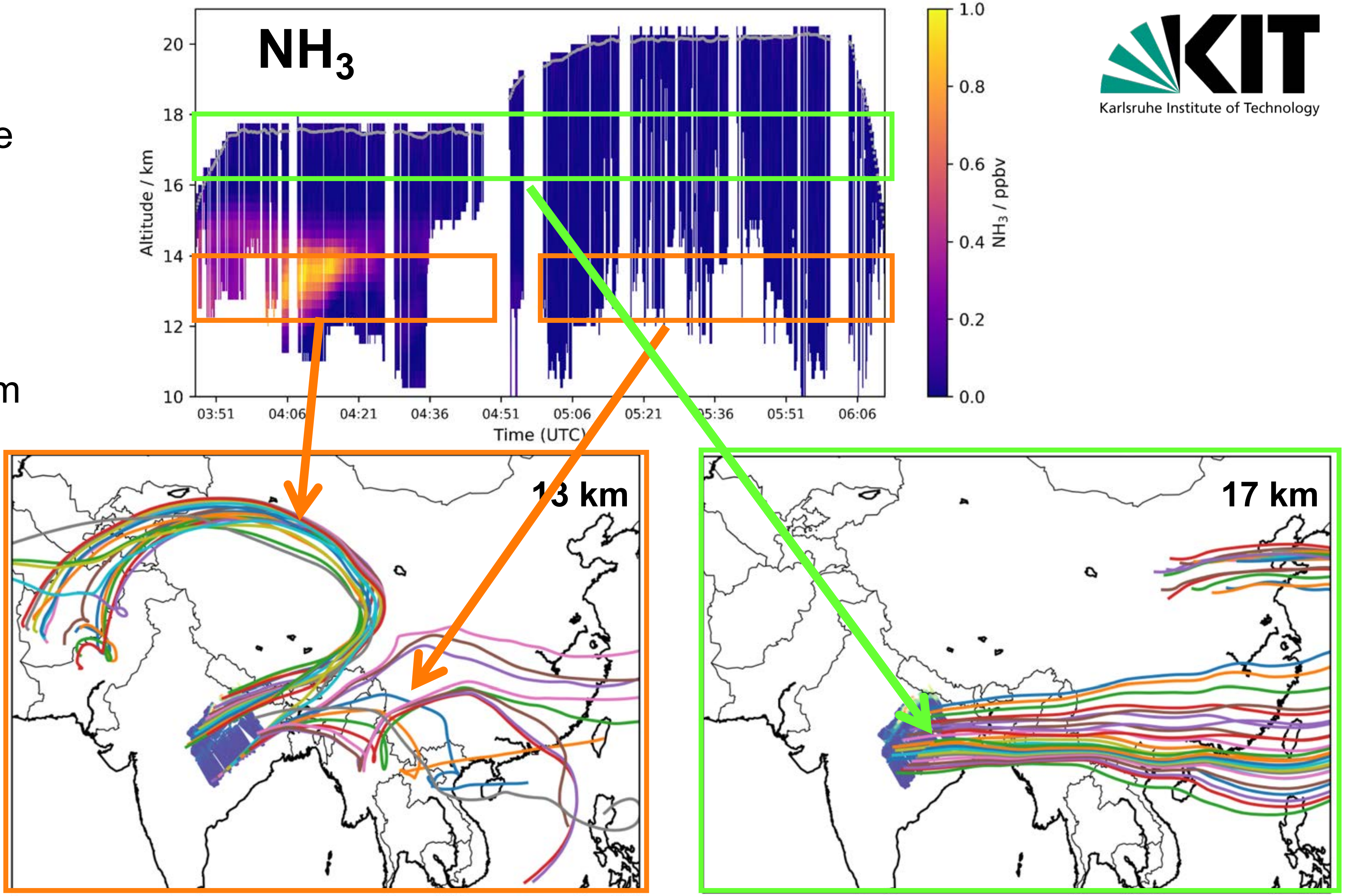
Cziczo & Abbatt (2000)
NH_4NO_3: strong inhibition to efflorescence down to 2% RH (298 – 238 K)
Aerosol flow tube equipped with FTIR spectrometer

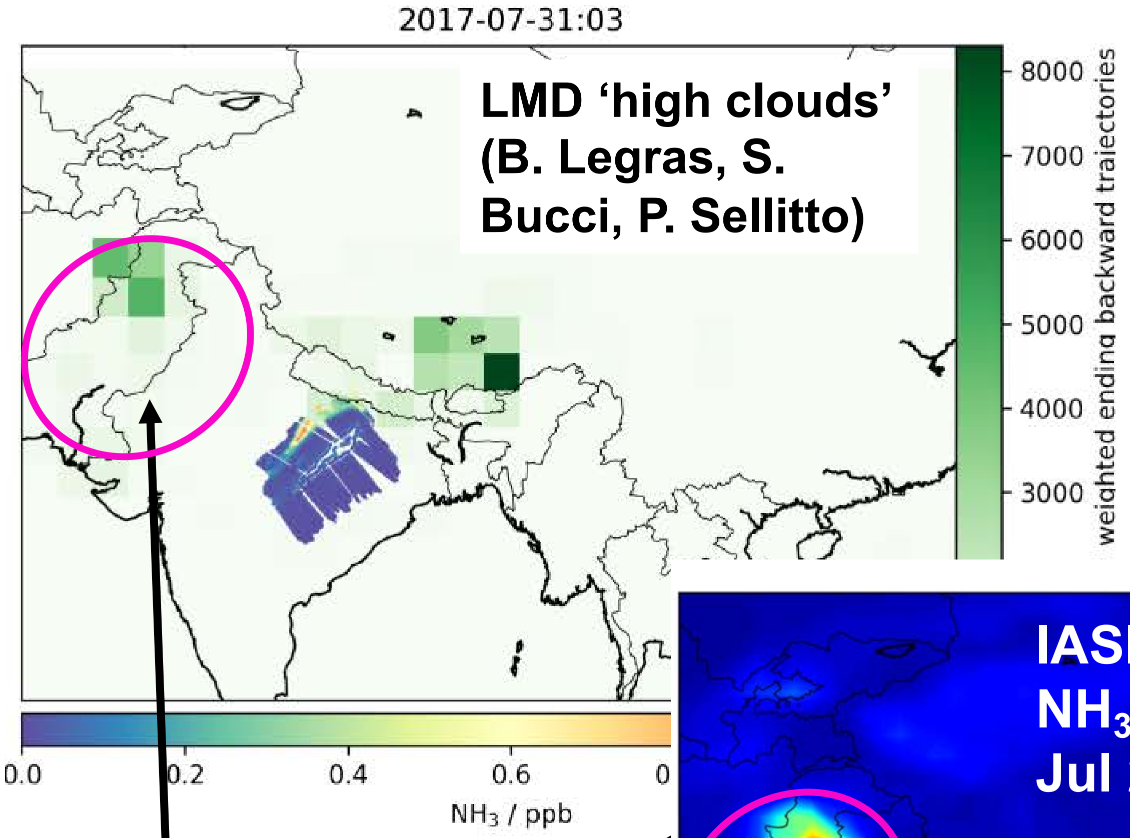


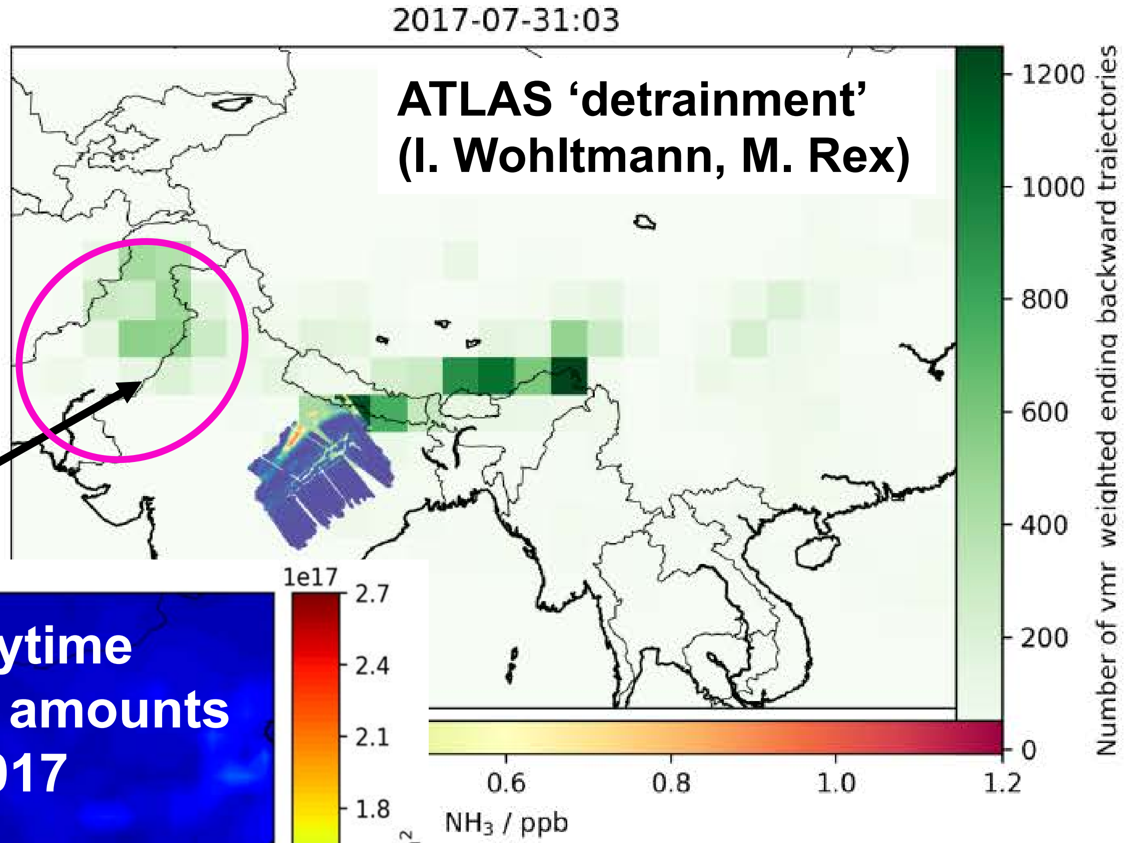
Deliquescence point:
61% RH

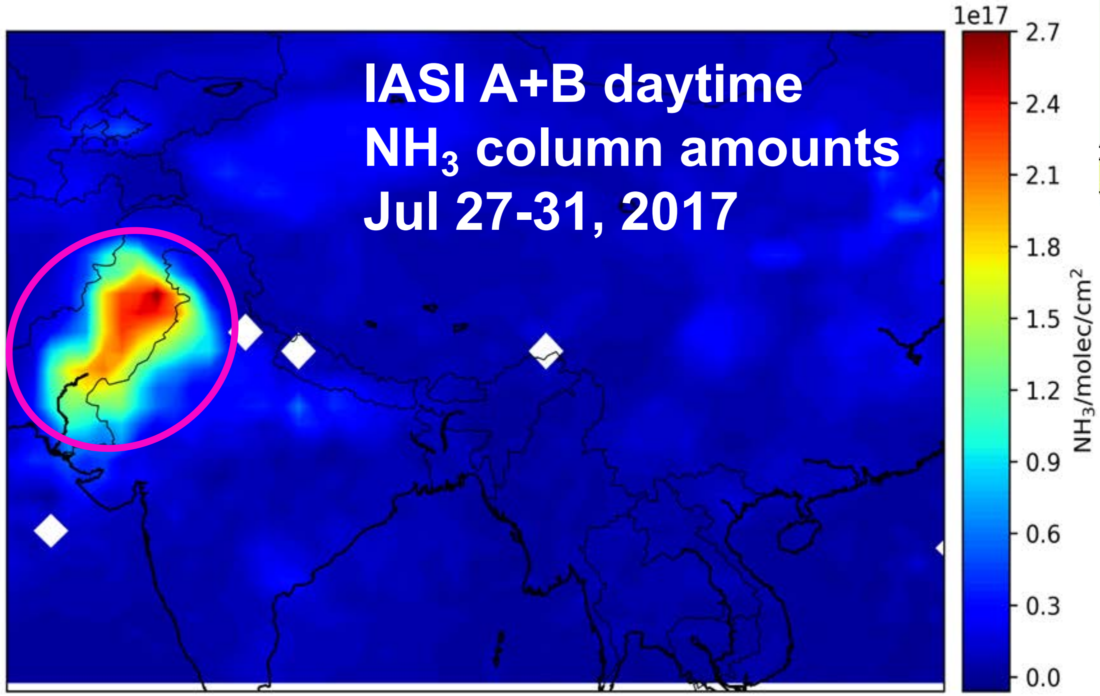
Backtrajectories 2017-07-31

- Different origin of the air encountered on the southbound vs. the northbound flight leg at 13 km altitude
- Same origin at 17 km









Density of backward trajectories originating at position of convection weighted by the observed NH_3 concentrations

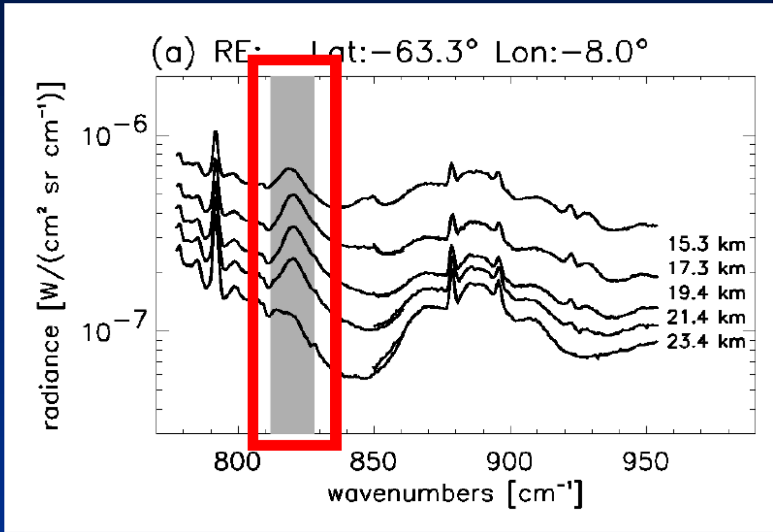
http://iasi.aeris-data.fr/NH3
The data produced at Université Libre de Bruxelles (ULB) by Simon Whitburn and Martin Van Damme
Van Damme et al., AMT, 2017

CRISTA and MIPAS observations of Polar Stratospheric Clouds: a peak at 820 cm^{-1}

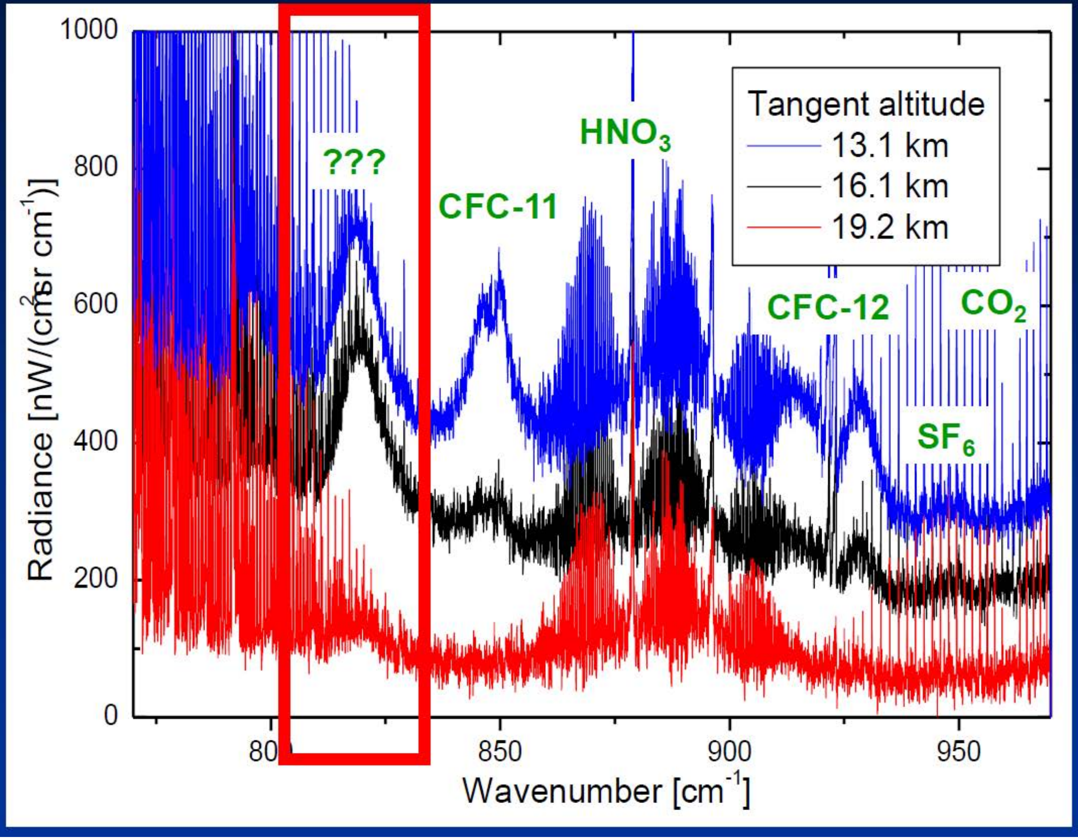
CRISTA PSC observations in August 1997

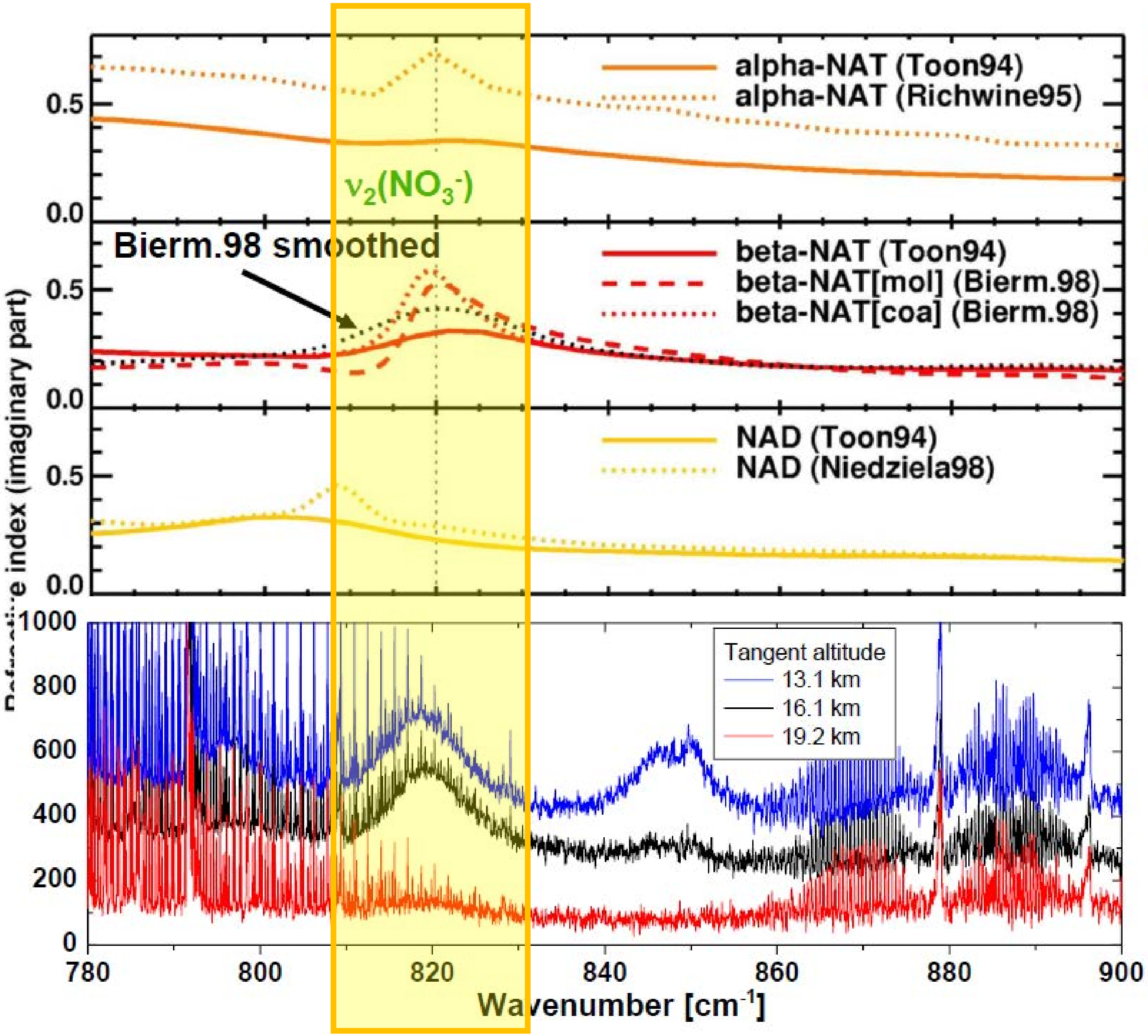
Spang and Remedios, 2003:

Spectral feature around 820 cm^{-1} attributed to NAT indirectly by HNO_3-temperature relationship and occurrence temperature of the band



MIPAS PSC observations over McMurdo on 4 Aug 2003





Atmos. Chem. Phys., 6, 1201–1219, 2006
www.atmos-chem-phys.net/6/1201/2006/

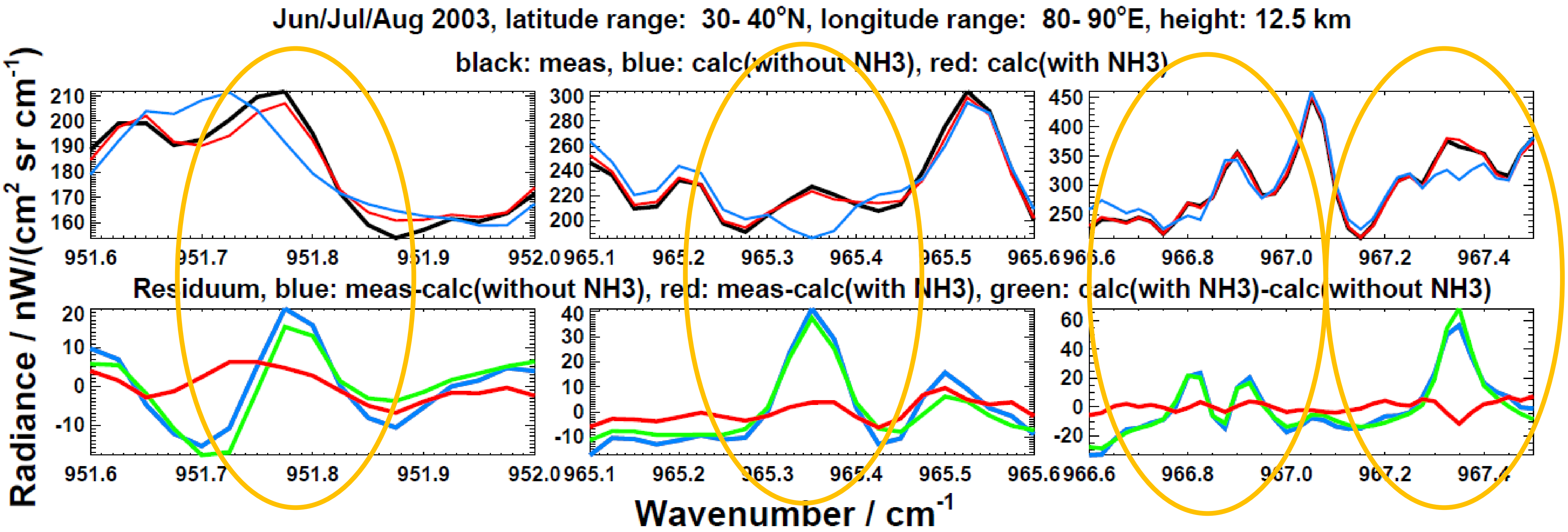
Atmospheric Chemistry and Physics

Spectroscopic evidence for NAT, STS, and ice in MIPAS infrared limb emission measurements of polar stratospheric clouds

M. Höpfner[1], B. P. Luo[2], P. Massoli[3,*], F. Cairo[3], R. Spang[4], M. Snels[3], G. Di Donfrancesco[5], G. Stiller[1], T. von Clarmann[1], H. Fischer[1], and U. Biermann[6,**]

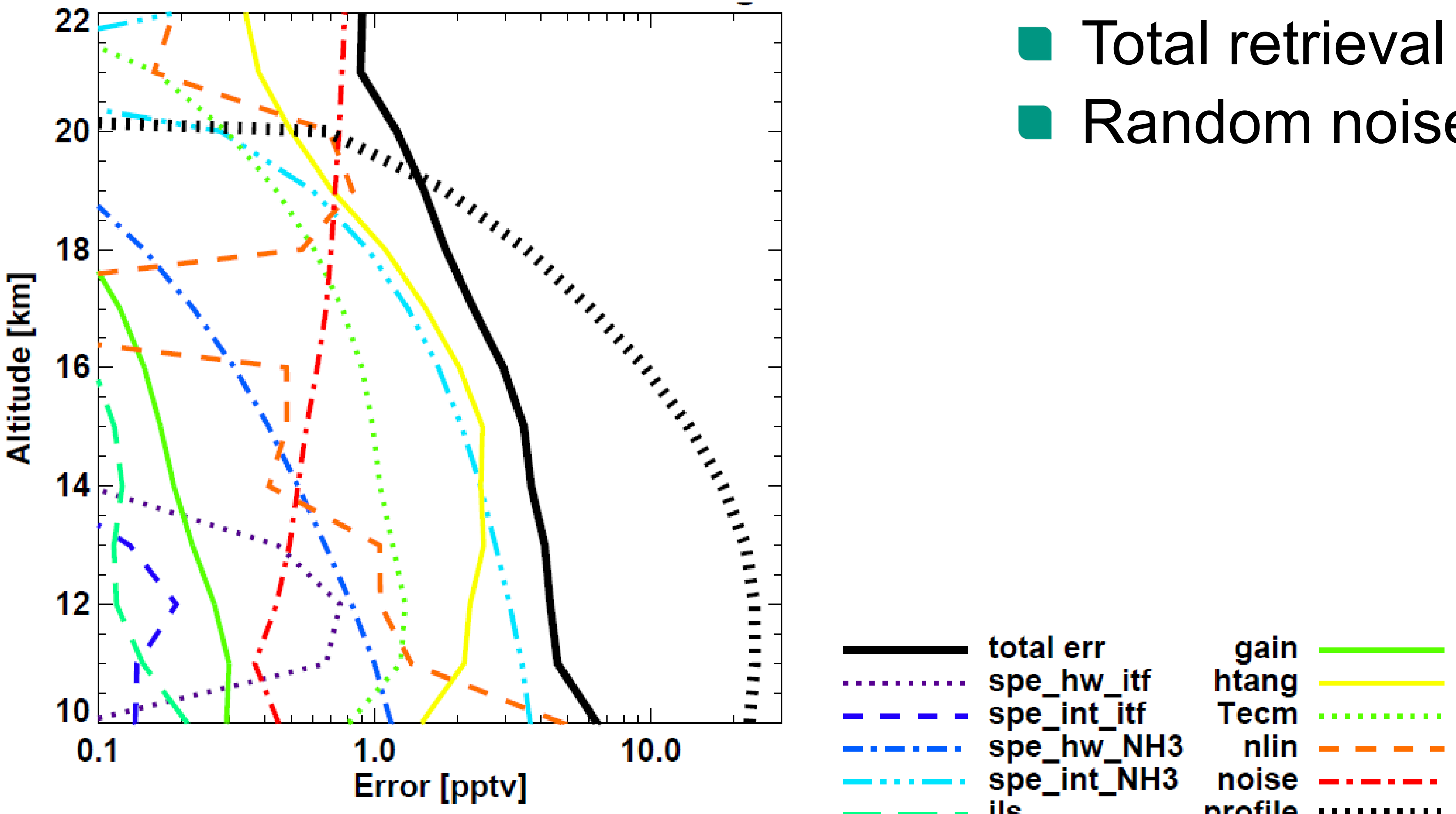
- Infrared signature at 820 cm^{-1} explained as the $\nu_2(NO_3^-)$ band of β-NAT

Spectral evidence for NH_3 in the Asian monsoon upper troposphere



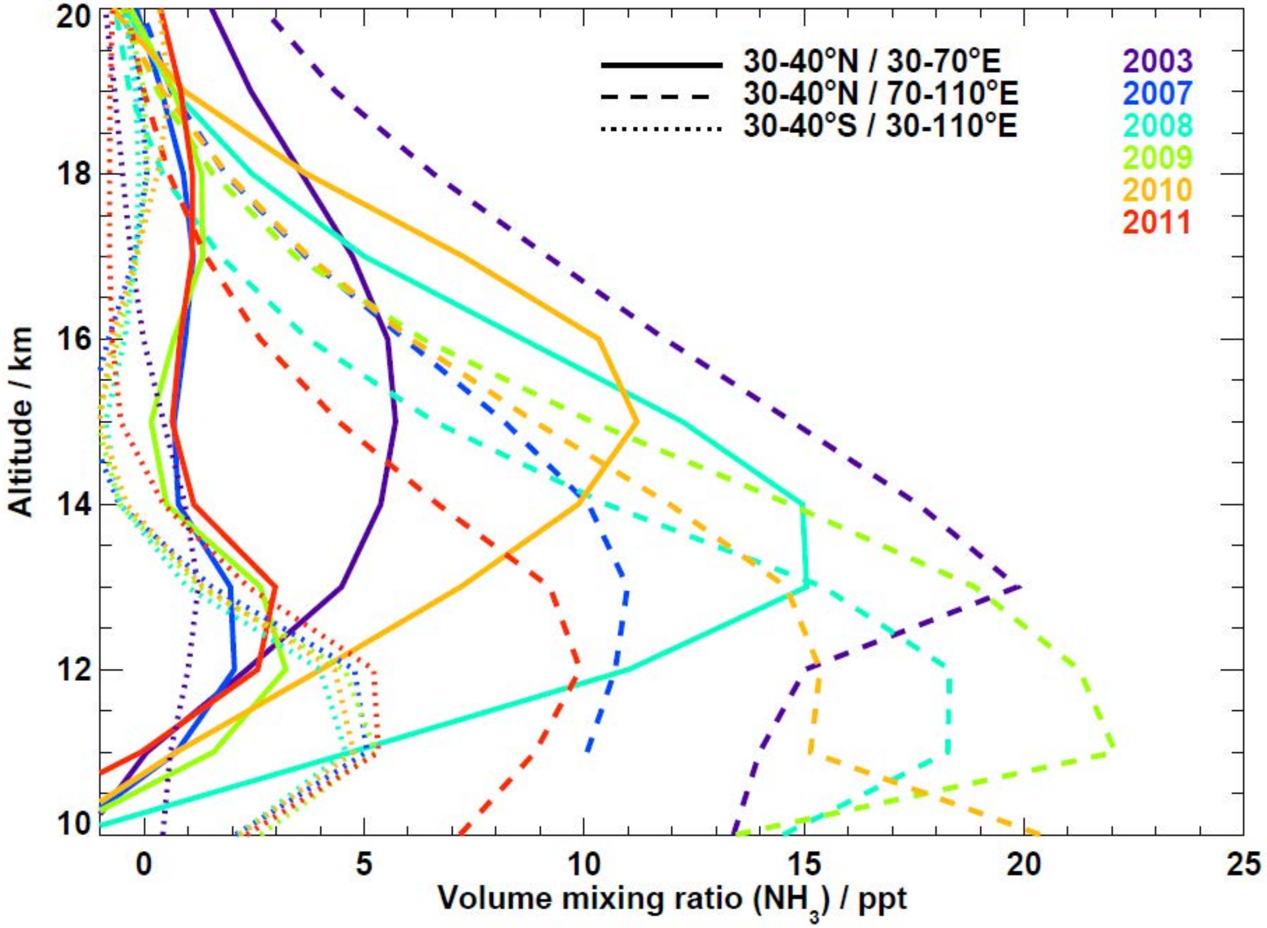
- Clear spectral residuals at position of NH_3 lines
- Strong reduction of spectral residuals when NH_3 is considered

NH_3 retrieval error estimation



- Total retrieval error ~ 5 ppt
- Random noise error ~1 ppt

NH_3 profiles within the Asian monsoon

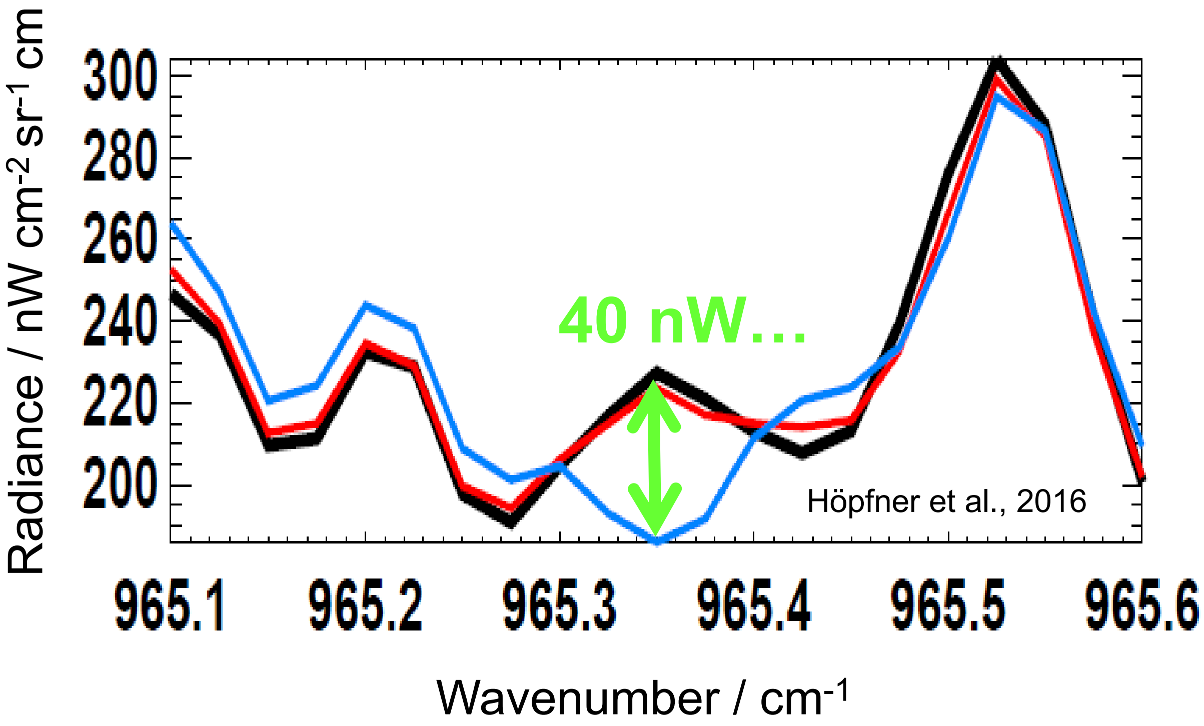


- NH_3 maximum larger and at lower altitudes in the eastern part of the monsoon area
- Much more variable and peaking at higher altitudes in the western part
- Maximum in southern hemisphere indicates detection limit of ~5 ppt

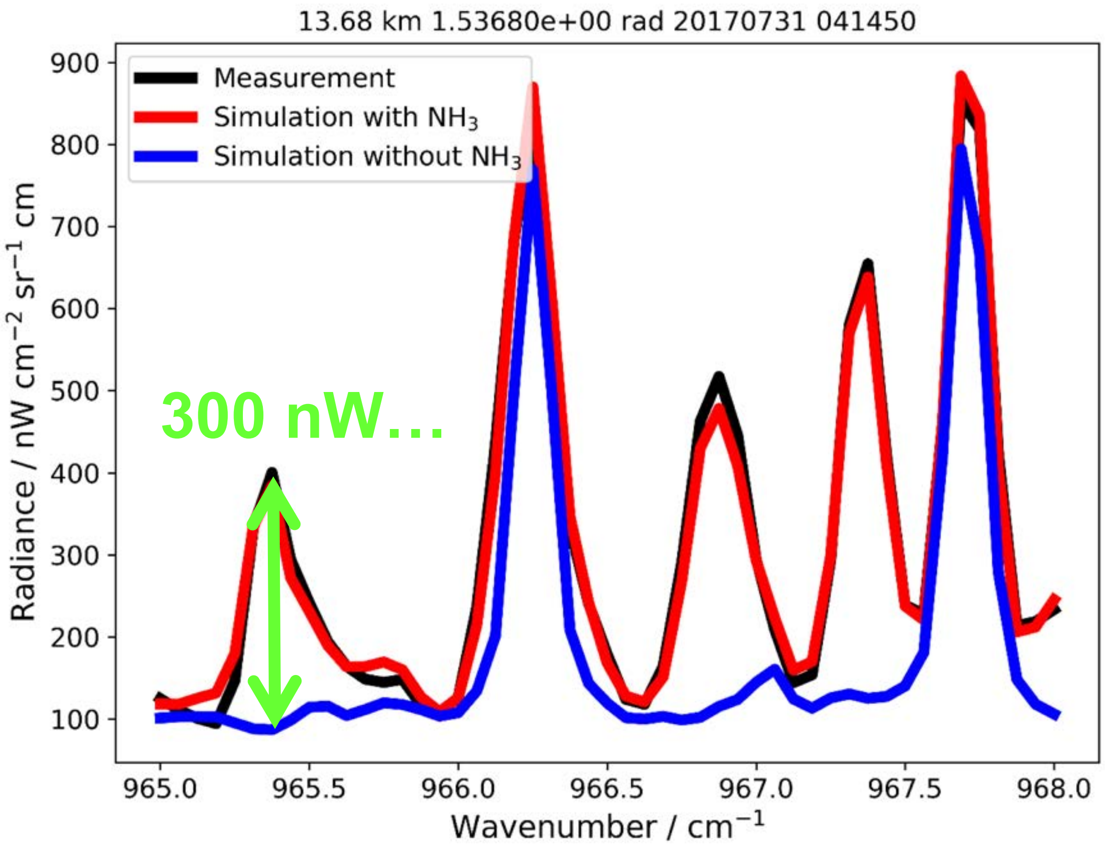
Spectral detection of NH_3

Karlsruhe Institute of Technology

MIPAS/Envisat

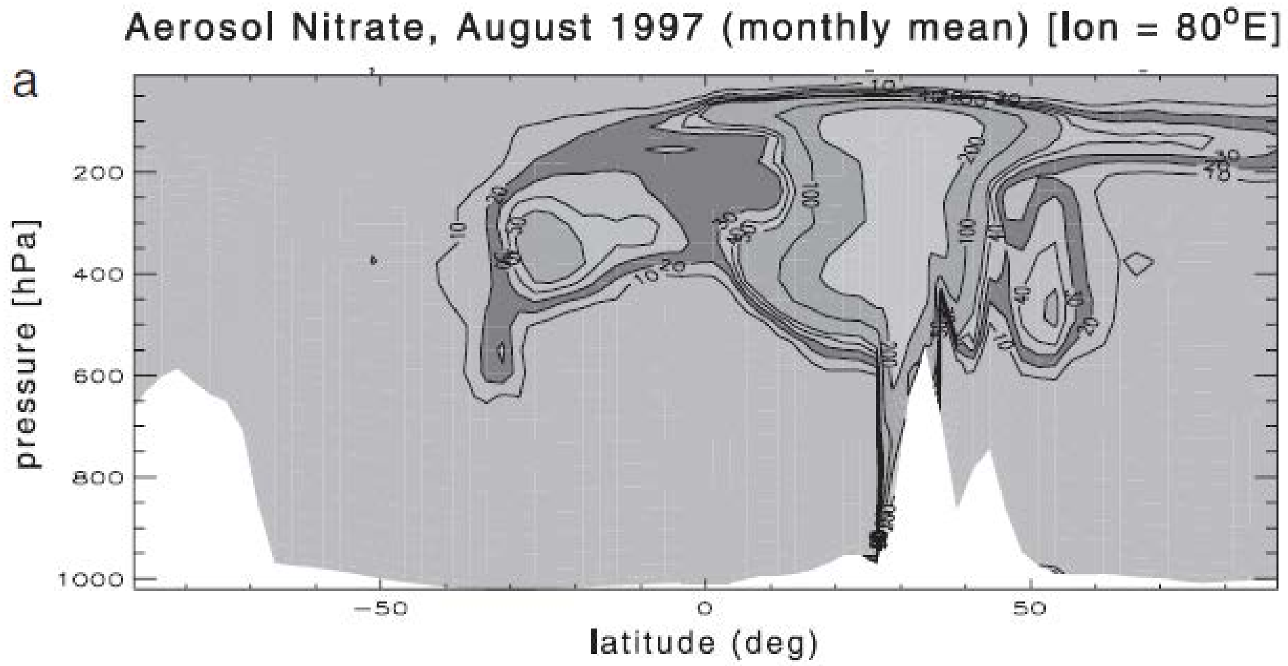


GLORIA/Geophysica



NH_3 and the Asian Tropopause Aerosol Layer

- Model simulates extended plume of ammonium nitrate in the upper troposphere
- Aerosols formed in the UT through neutralization of nitric acid (in the model present in higher amounts than sulfuric acid) by a surplus of NH_3



Metzger et al., JGR, 2002