PSC Complexity: The underlying problem in PSC research

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Three PSC questions need to be answered:

1. What are PSCs made of?
2. How do PSCs form?
3. How do PSCs grow?

The answers to these questions may be more complicated than we would like... especially because of NAT “rocks”

Question 1: What are PSCs made of?

Standard classification:

- Type II PSCs: Water ice **OK**
- Type I PSCs: Nitric acid **OK**
  - ~~Type 1a = solid-phase, probably NAT~~
  - ~~Type 1b = liquid, supercooled ternary solu~~tions (STS)

And then there are all the other types:

~~1a enhanced, 1c, 1d, 1m, 1x, ….~~

Why doesn't this classification system work?

1a PSCs are NOT pure NAT, 1b PSCs are NOT pure liquid!

What are Type I PSCs <u>really</u> made of?

Both liquid and solid particles are simultaneously present in all Type I PSCs

The ratio of liquid to solid can be any value from 0 and 1

"1a" and "1b" are just two extremes of a smoothly varying spectrum

- The dividing lines are arbitrary and depend on instrument capabilities

Solid particles are NAT (in all likelihood)

NAT has been found in stratosphere [Voigt et al., 2000, Schreiner et al., 2003]

NAD is probably not an important component of PSCs

- no stratospheric measurements of NAD (only lab data)
- competition with NAT and STS severely limit its importance even if present [McKinney et al., 2004]

Evidence for STS/NAT mixtures

1) NAT particles may be present whenever $T<T_{NAT}$

- ER-2 NAT rocks nearly ubiquitous [Northway et al., 2002]
- VINTERSOL measurements also show widespread NAT rocks

… but NAT particles may not always be detectable

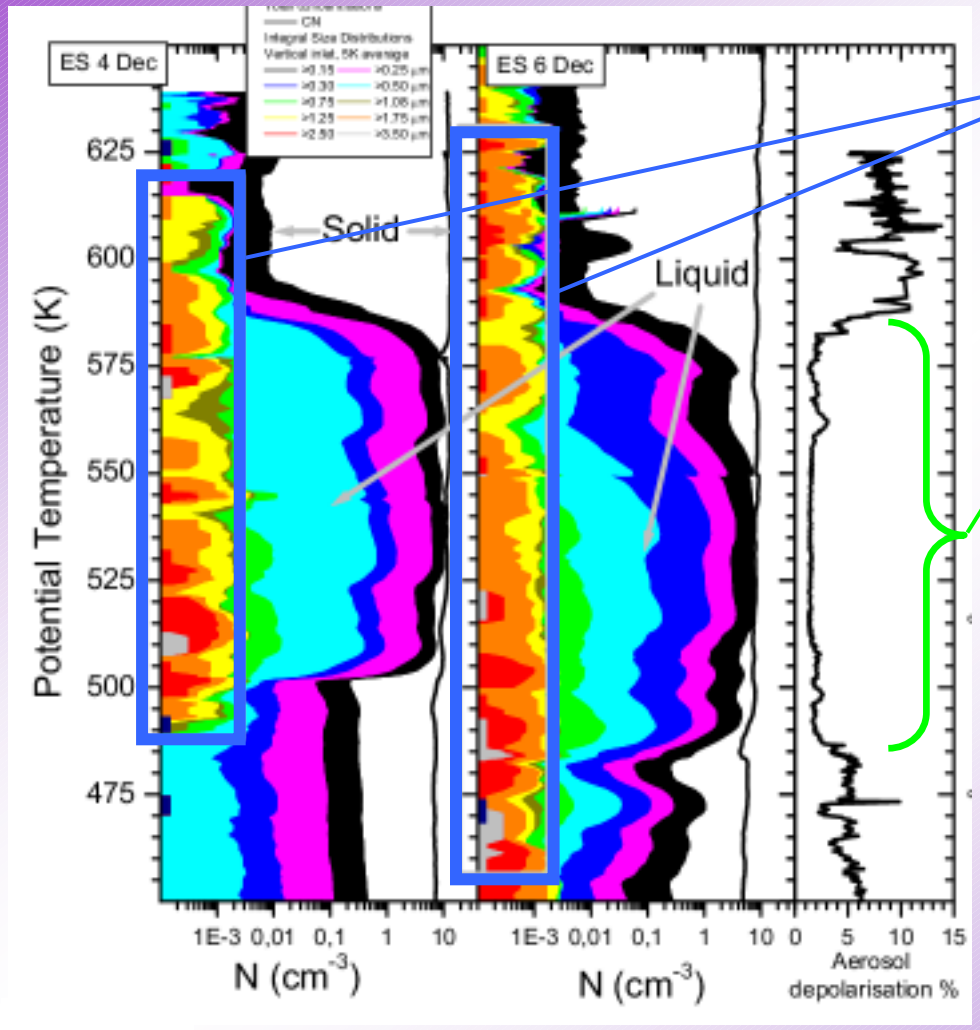
- Liquid particles can mask NAT particles [Larsen et al., *ACPD*, 2004]
- NAT particle concentration may be small ($<10^{-4}$) [Northway et al., 2002]

The actual extent of NAT particles is currently a critical uncertainty

2) Most particles remain liquid throughout winter [Drdla et al., 2002]

- If <0.1% of particles are NAT, remaining 99.9% are liquid
- Type 1b clouds are observed even at end of winter

Liquid particles can mask NAT particles



Size distributions show NAT particles present throughout profile

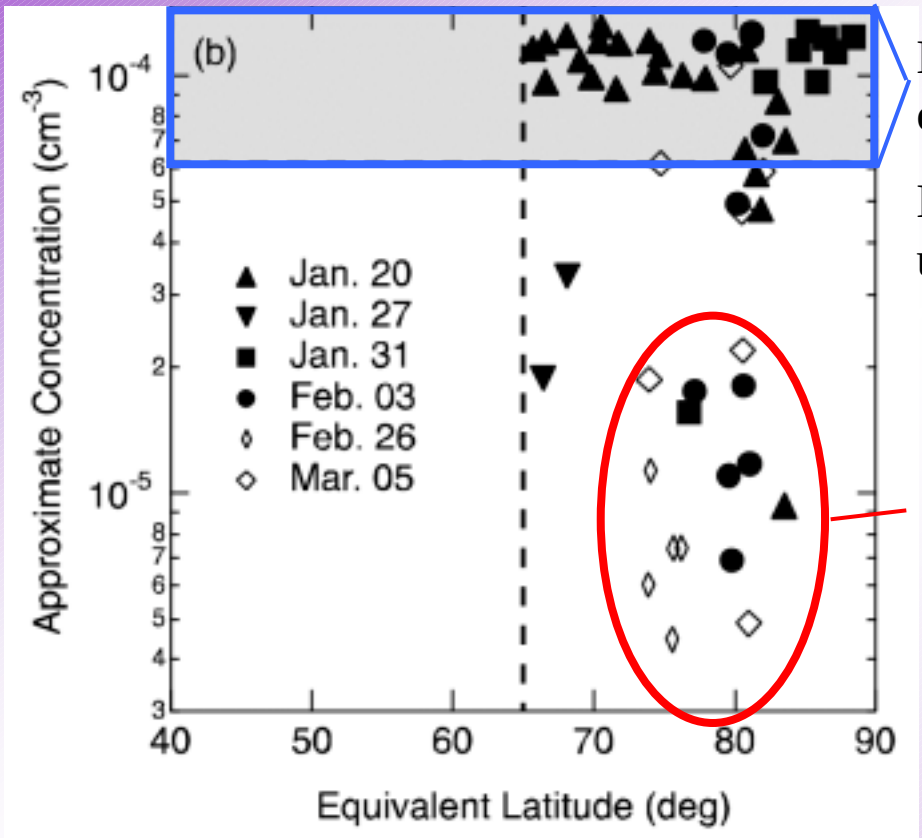
But depolarization data does not pick up NAT particles when liquids are dominant –

Liquid particles hide NAT particles

Larsen et al., *ACPD* [2004]

NAT Concentrations can be very small

1.e-4 is NOT a “canonical” NAT rock concentration. Actual range ~4.e-6 to ~5.e-3



NO_y measurements underestimate concentrations >6.e-5

MASP measurements show concentrations up to 5.e-3 [Brooks et al., 2003]

NO_y measurements show concentrations as low as 4.e-6

MASP and traditional particle counters can not measure <1.e-4, so these NATs have been missed in the past

Northway et al. [2002]

Why are NAT/STS mixtures surprising?

NAT is always thermodynamically favored over STS

STS and NAT can only coexist if NAT is not in equilibrium

NAT non-equilibrium is a consequence of NAT “rocks”

- Small concentrations of NAT particles have a small surface area, limiting growth rate
- Liquid particles always have large surface area, allowing equilibrium to be established within an hour

NAT is thermodynamically favored

STS is kinetically favored

NAT rocks take days to equilibrate

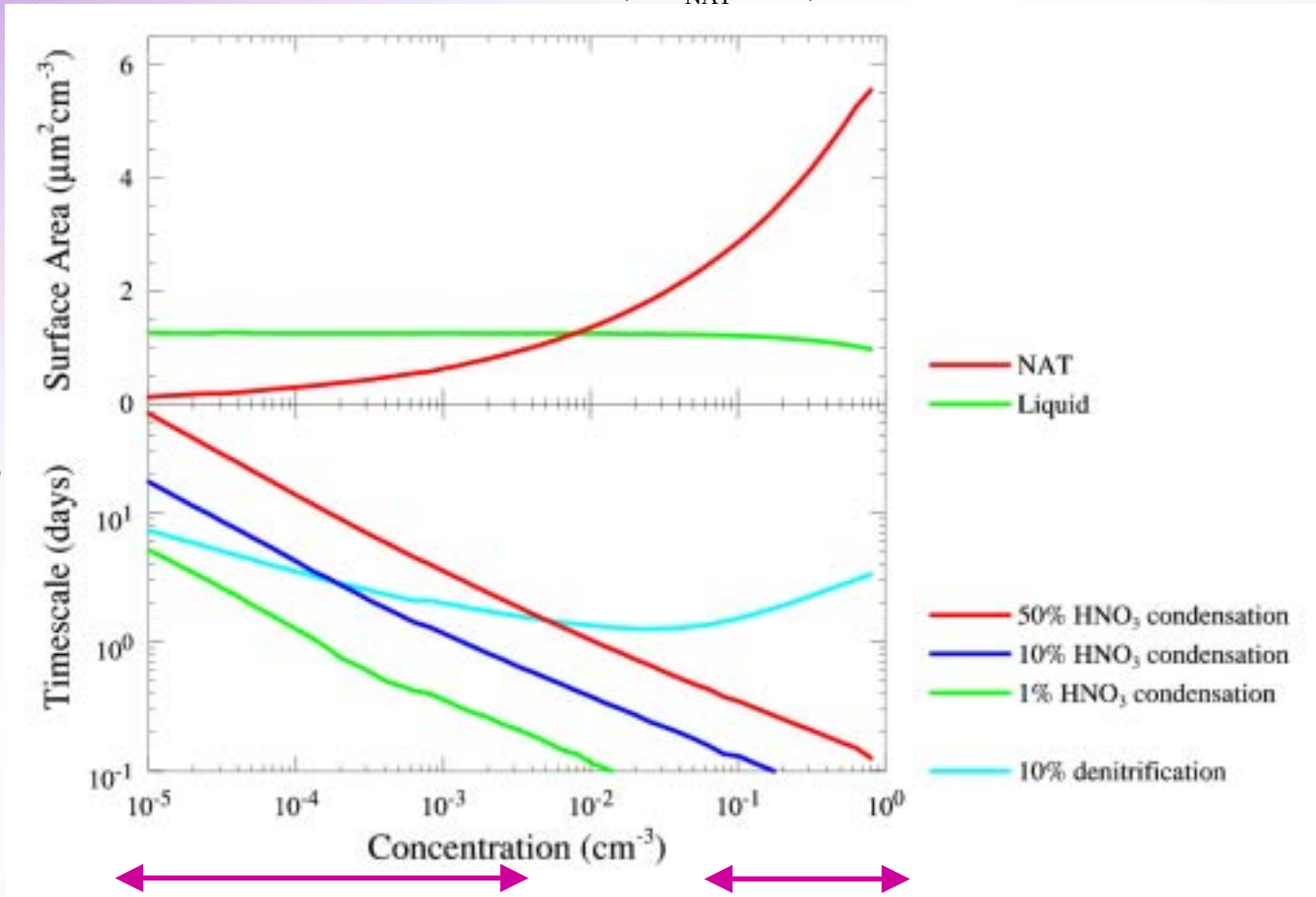
Model calculations at 192 K ($T-T_{NAT}$=-3K)

"NAT rock" surface areas always smaller than liquid:

NAT is unimportant for heterogeneous chemistry

The smaller the concentration, the longer it takes for HNO_3 condensation

Particles will sediment before they reach maximum size



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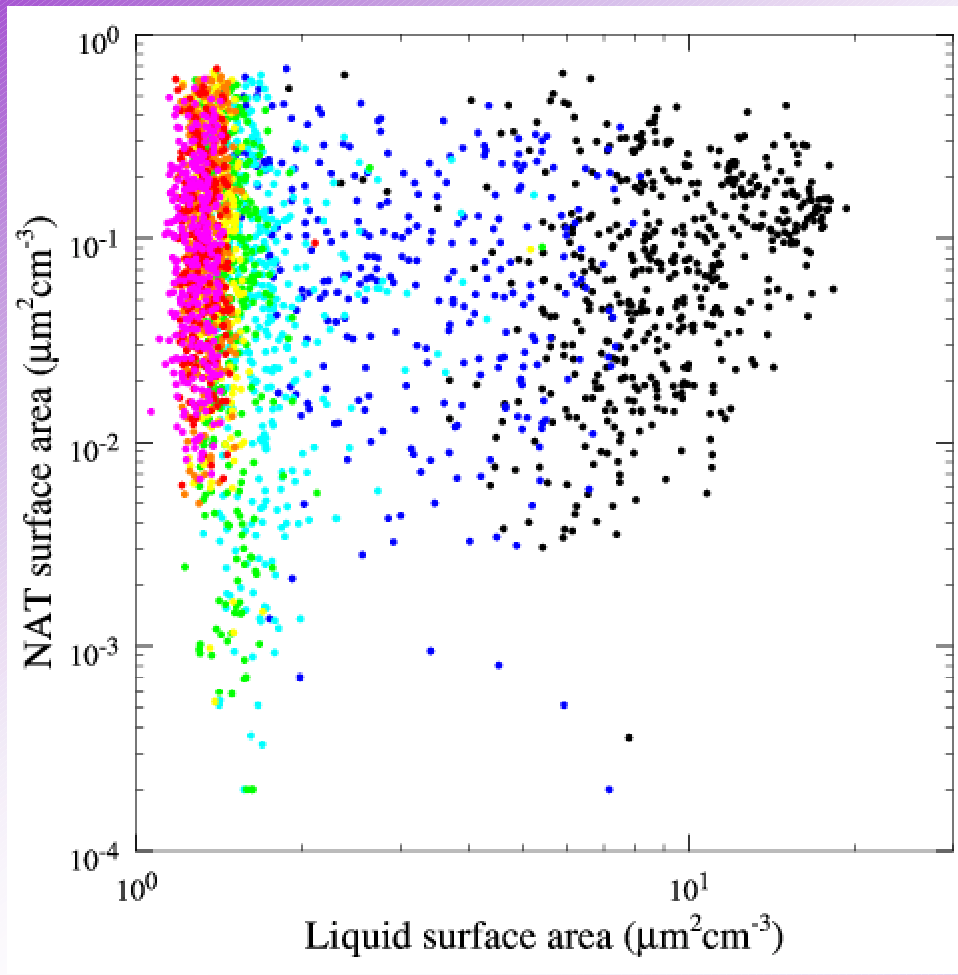
Model results: PSC surface areas



IMPACT model simulation of 1999-2000 winter with small (2.e-3) NAT number

[HetFrzB scenario from Drdla et al., 2002]

Liquid surface areas are much larger than NAT surface areas

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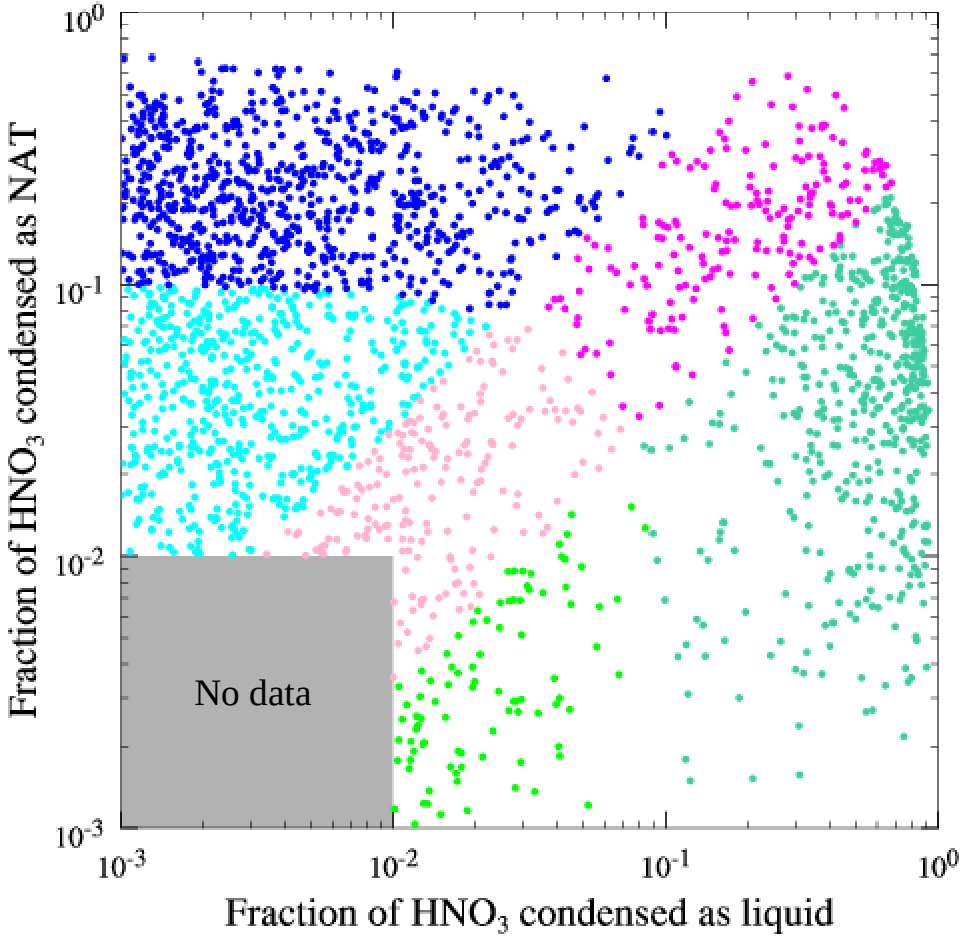
Model results: HNO_3 content



Mixed, strong (3.4%)
Mixed, weak (3.5%)
NAT, strong (16.4%)
NAT, weak (13.4%)
Liquid, strong (9.1%)
Liquid, weak (2.2%)

HNO_3 content provides a microphysically based PSC definition

Any ratio of NAT to liquid is possible – continuum of PSC characteristics

When distinct populations do not exist, any classification scheme is arbitrary

But what do these PSCs look like to satellites?

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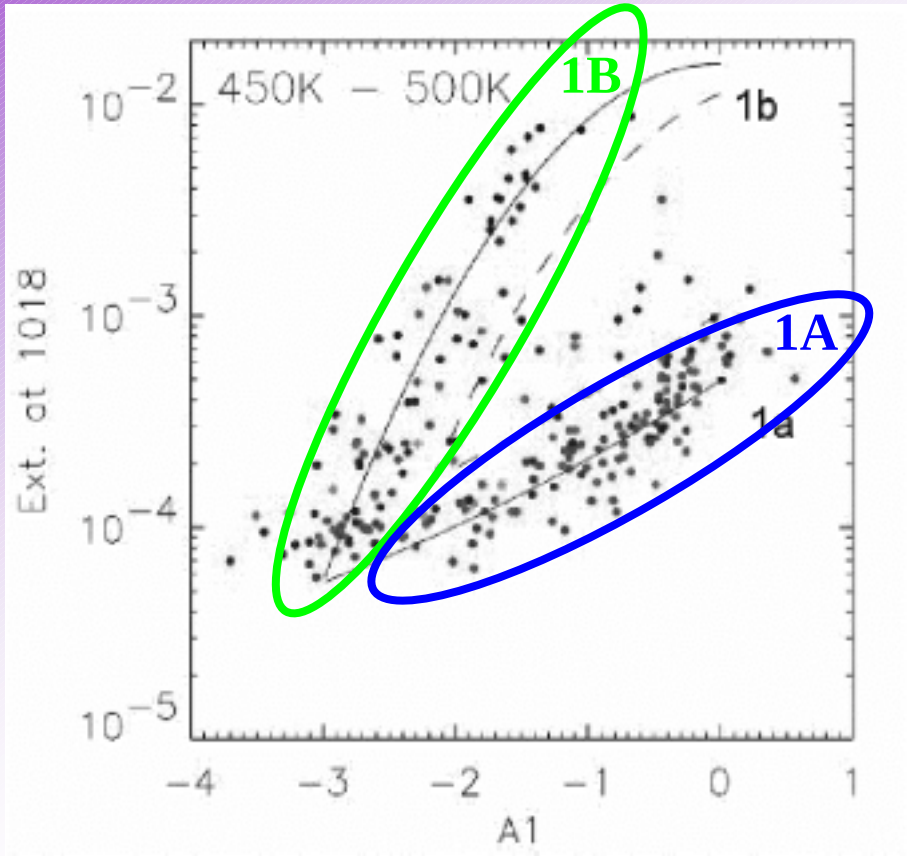
Satellite 1a/1b PSC discrimination

traditional PSC detection channel:
Extinction



Wavelength dependence

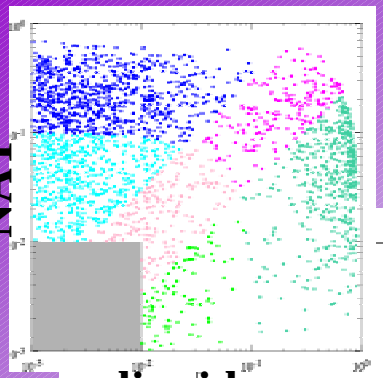
provides particle size information

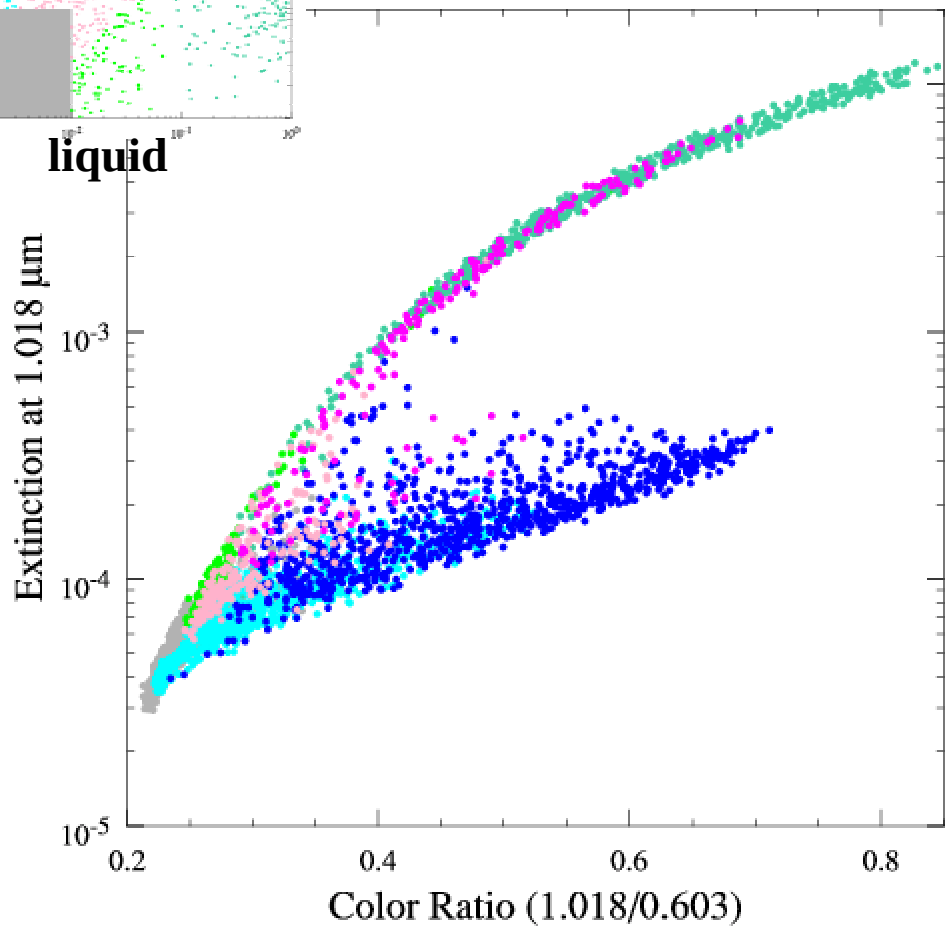
Two populations of PSCs are apparent

- Upper branch matches modeled liquid (STS) growth curve = **1B PSCs**
- Lower branch requires presence of large particles, i.e., NAT = **1A PSCs**

Strawa et al. [2002, 2004]

Model results: extinction





Model liquid clouds do fall on 1b curve, model NAT clouds on 1a curve

But correspondence is imperfect:

Type 1b PSCs can contain significant NAT – liquid particles are masking solid ones

All the categories overlap substantially

- Mixed, strong (3.4%)
- Mixed, weak (3.5%)
- NAT, strong (16.4%)
- NAT, weak (13.4%)
- Liquid, strong (9.1%)
- Liquid, weak (2.2%)
- No PSC (52.0%)

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Summary: PSC composition

"1a is NAT, 1b is STS" is an oversimplification

- More likely that NAT and liquid are both present in almost all PSCs

1a/1b discrimination is useful

- NAT and liquid clouds behave differently
- But need to be aware of limitations:
  - 1a/1b definition is arbitrary and measurement-dependent
  - All measurements, especially remote, need to better define detection limits so that different measurements can be meaningfully intercompared

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Question 2: How do PSCs form?

There is no <u>one</u> PSC formation process

As many as four freezing mechanisms may contribute to NAT formation:

1. NAT nucleation on water ice in leewaves
2. NAT nucleation on water ice at synoptic scale
3. Homogeneous freezing of NAT at $T-T_{NAT} \sim -5$ K
4. Heterogeneous freezing of NAT at $T-T_{NAT} > -5$ K

Formation mechanism controls temperature at which NAT forms and concentration of NAT particles

NAT concentration determines:

- Maximum particle surface area
- Maximum denitrification rate
- Growth time scale

NAT Nucleation on Ice

NAT nucleation on ice has been shown to occur in leewave clouds; same process should also occur on synoptic scale

NAT formation appears to be fairly well quantified

Widespread denitrification could occur below leewave-generated clouds

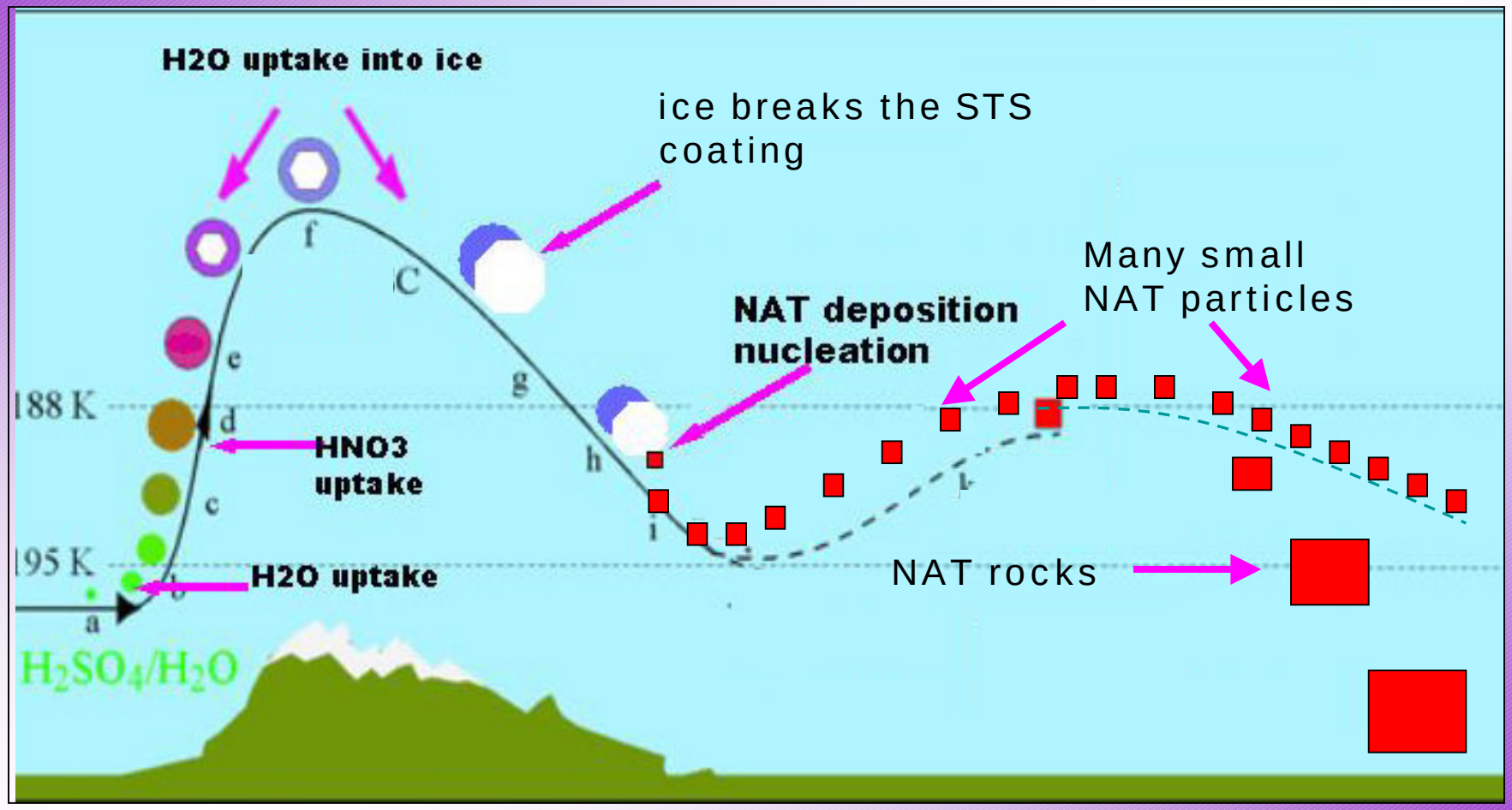
Largest uncertainty:

How common are leewave clouds?

- Scandinavian measurements may be biased by large number of leewaves that are generated over Scandinavian mountains
- Need large-scale statistics, not case studies

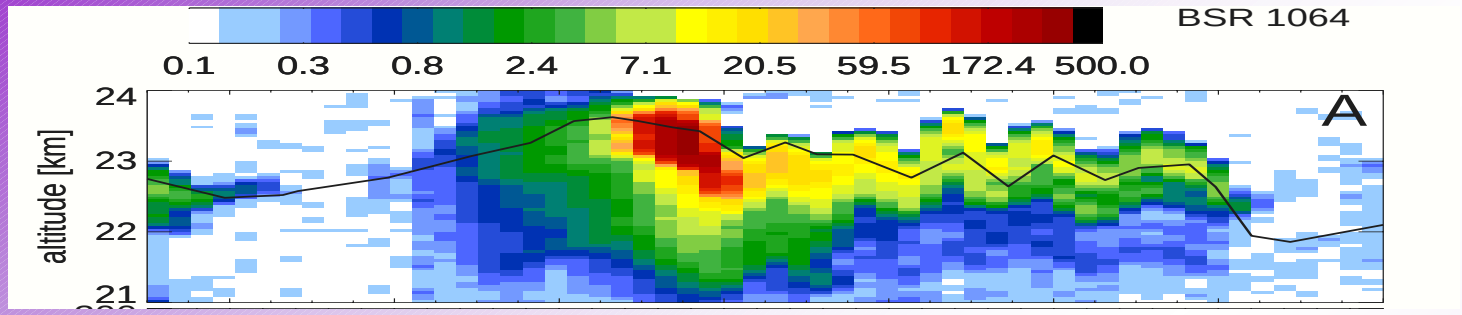
New DLAPSE model results show that up to 50% of the large-scale denitrification could be caused by mountain waves

PSC Evolution in Mountain Waves

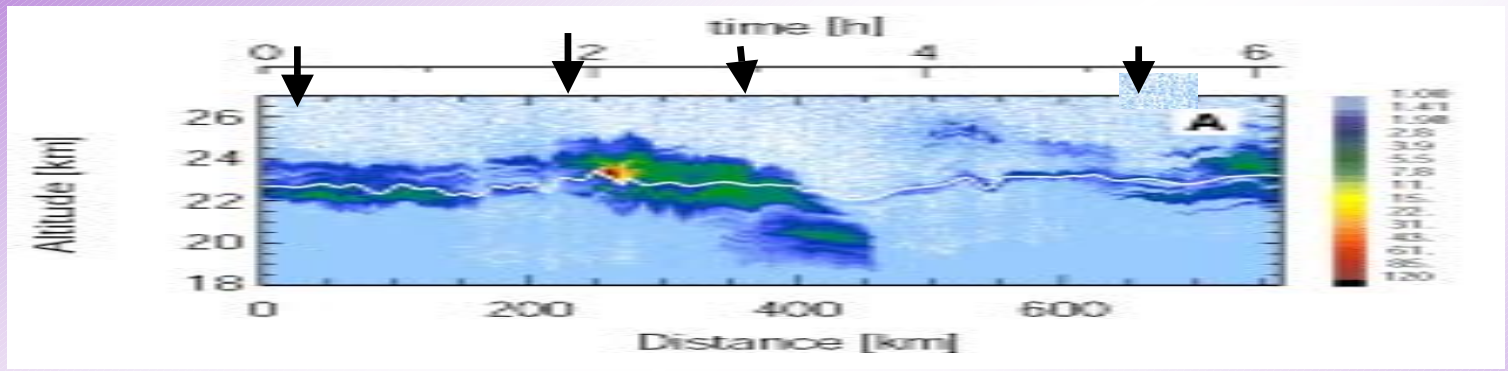


[B. Luo]

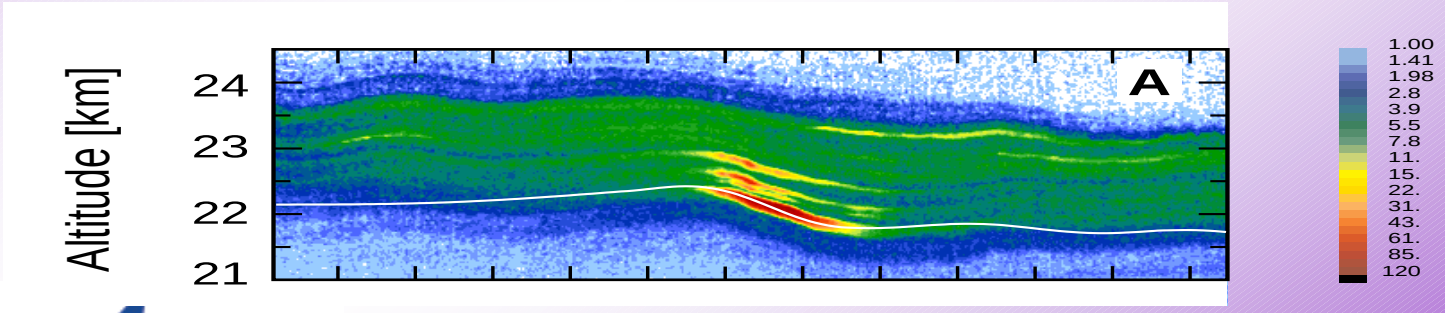
Mountain wave PSC observations



Many NAT



Less NAT



Few NAT

Carslaw et al., Tsias et al., Wirt et al., Luo et al.

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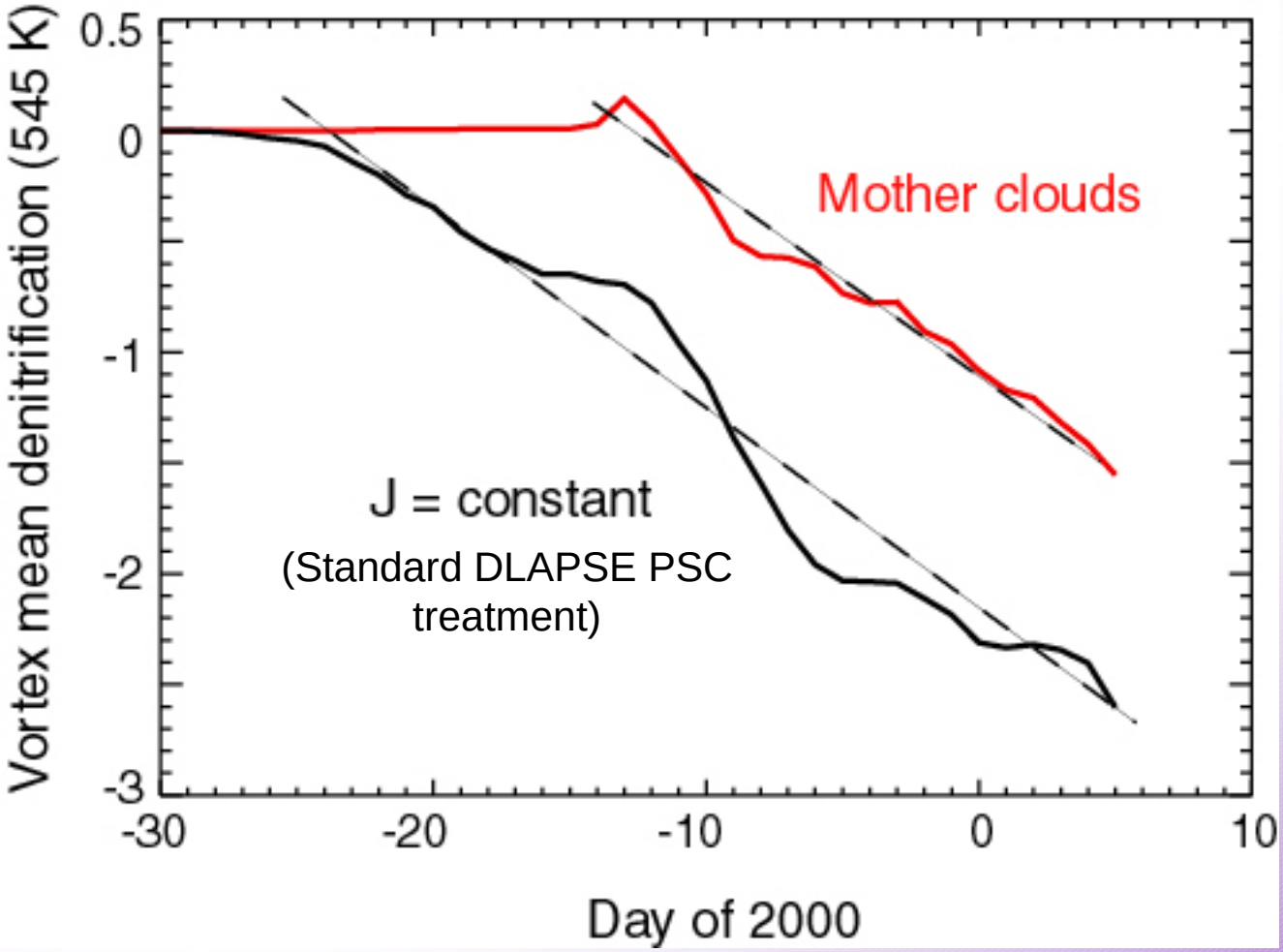
DLAPSE denitrification from leewave clouds



NAT PSCs generated by mountain waves have large NAT concentrations

BUT ~10^{-4} concentrations can develop below main cloud, causing denitrification: "mother cloud" theory

[Dhaniyala et al., 2002; Fueglistaler et al., 2003]

Mechanism has been tested in DLAPSE model [Mann et al., in prep]

[Mann et al., in prep]

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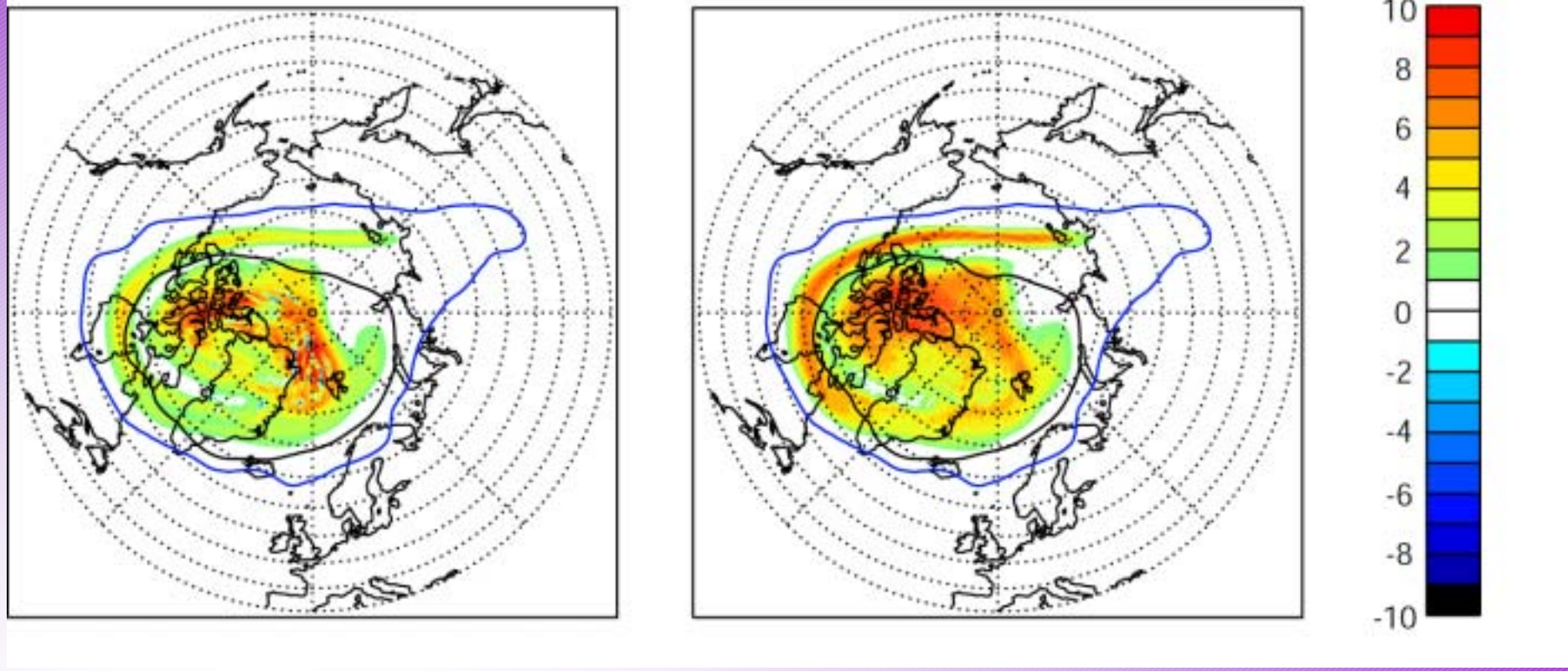
DLAPSE denitrification from leewave clouds



Vortex-mean denitrification due to Mother Clouds ~50-60% of J = constant case (snapshot on Jan. 6, 2000, 525 K) [Mann et al., in prep]

Homogeneous freezing

Primary source of laboratory data: Salcedo et al. [2001]

But applying measurements to stratosphere has several complications

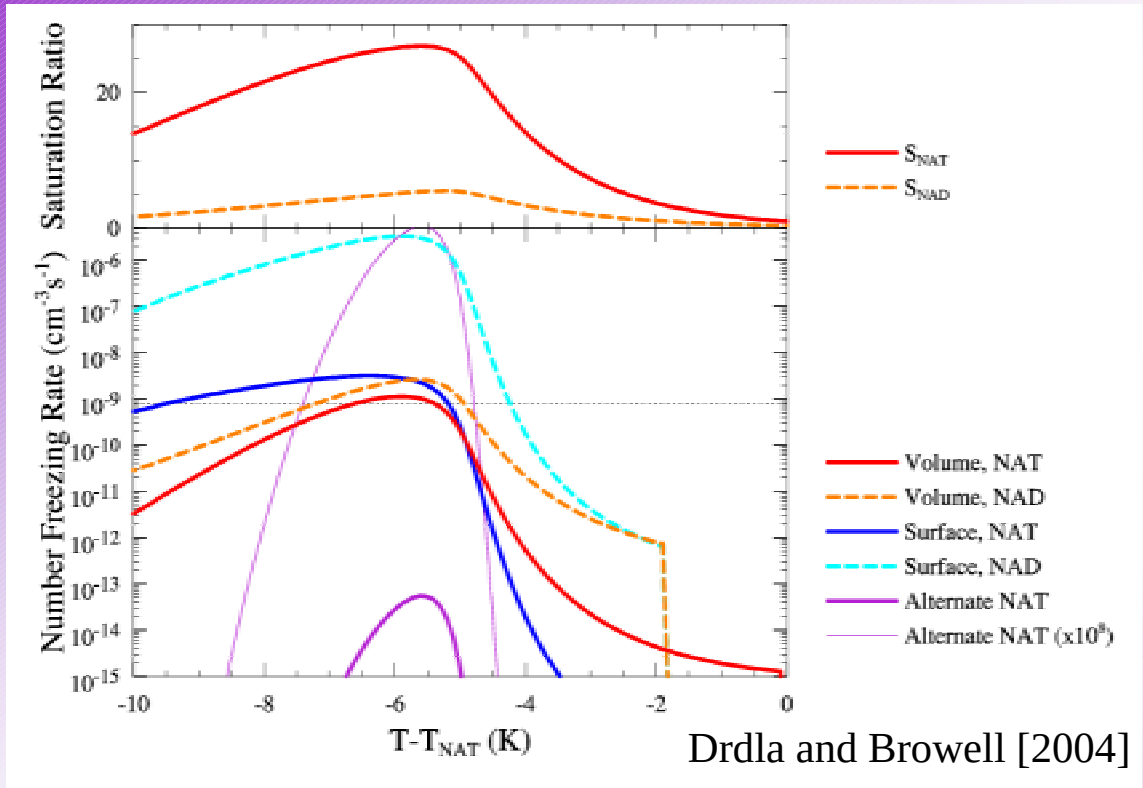
- Is freezing controlled by particle volume or surface area [Tabazadeh et al., 2002]
- How should data be extrapolated from lab conditions (S_{NAT}>50) to stratosphere, where S_{NAT}<30 [Knopf et al., 2002]
- Does freezing produce NAD or NAT (although NAD freezing does not imply NAD existence – NAD may rapidly transform into NAT)

Does homogeneous freezing explain data?

Sometimes [Irie et al., 2003; Larsen et al., 2004]

But does not explain 1a PSCs that are seen before 1b PSCs

Treatments of Homogeneous Freezing



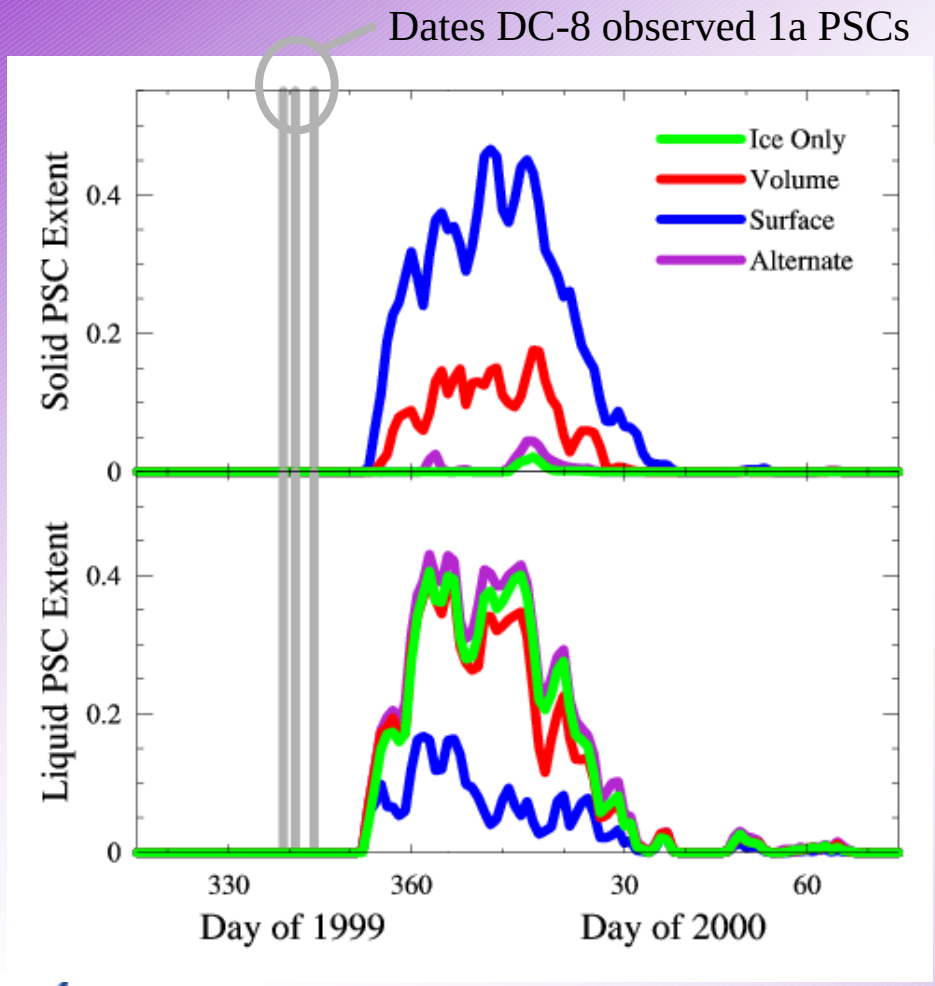
Drdla and Browell [2004]

Comparison of multiple possible treatments of homogeneous freezing

All treatments of homogeneous freezing produce freezing rates that are dependent on S_{NAT}

- Freezing only effective when $T-T_{NAT}<-4$, max at $T-T_{NAT}\sim-5.5$ ("freezing belt", Tabazadeh et al., 2001])
- PSC evolution must always be 1b <u>then</u> 1a

Characteristics of Homogeneous Freezing



Drdla and Browell [2004]

Homogeneous freezing can produce solid-phase PSCs, at least in 1999-2000 winter

But solid-phase PSC onset date is always after Dec. 15, much later than observed PSC onset (DC-8, POAM)

Formation of early December PSCs is difficult to explain:

- Not leewave-generated [Pagan et al., 2004]
- No synoptic-scale ice
- Not homogeneous freezing

What is left?

Heterogeneous Freezing

Primary justification for heterogeneous freezing:

Other freezing mechanisms don't work (at least not for all observed PSCs)

Heterogeneous freezing is enhanced freezing, caused by particulate impurities

- can coexist with homogeneous freezing (although homogeneous freezing could be too slow to be stratospherically relevant)
- nuclei are completely unknown (composition, concentration, efficiency)
- probably can not identify nuclei without in situ measurements (even with in situ measurements, identification will be challenging)
- satellite data can help to map out NAT particle concentrations
  - empirically determine key parameters that control heterogeneous freezing (concentration, temperature barrier, etc.)
  - most important measurements are those where heterogeneous freezing is only possible mechanism (early winter, upwind, high altitude)

PSC Formation: Summary

Process:	Temperature required	Rate known?	Contribution to denitrification	Key uncertainty
Ice	$T<T_{ice}$-3 (synoptic)	yes	<1% [Drdla et al., 2002]	
Leewave	$T<T_{ice}$-3 (mesoscale)	yes	up to 50% [Mann et al.]	Leewave climatology
Homogeneous	$T<T_{NAT}$-4	some data	**?**	Extrapolating lab data to stratosphere
Heterogeneous	Unknown ($T<T_{NAT}$-2?)	no	**?**	Identifying nucleus

Question 3: How do PSCs grow?

Traditional approximation: All PSCs are in equilibrium

Liquid particles are indeed in equilibrium (at synoptic scale)

But NAT rocks are <u>not</u> in equilibrium

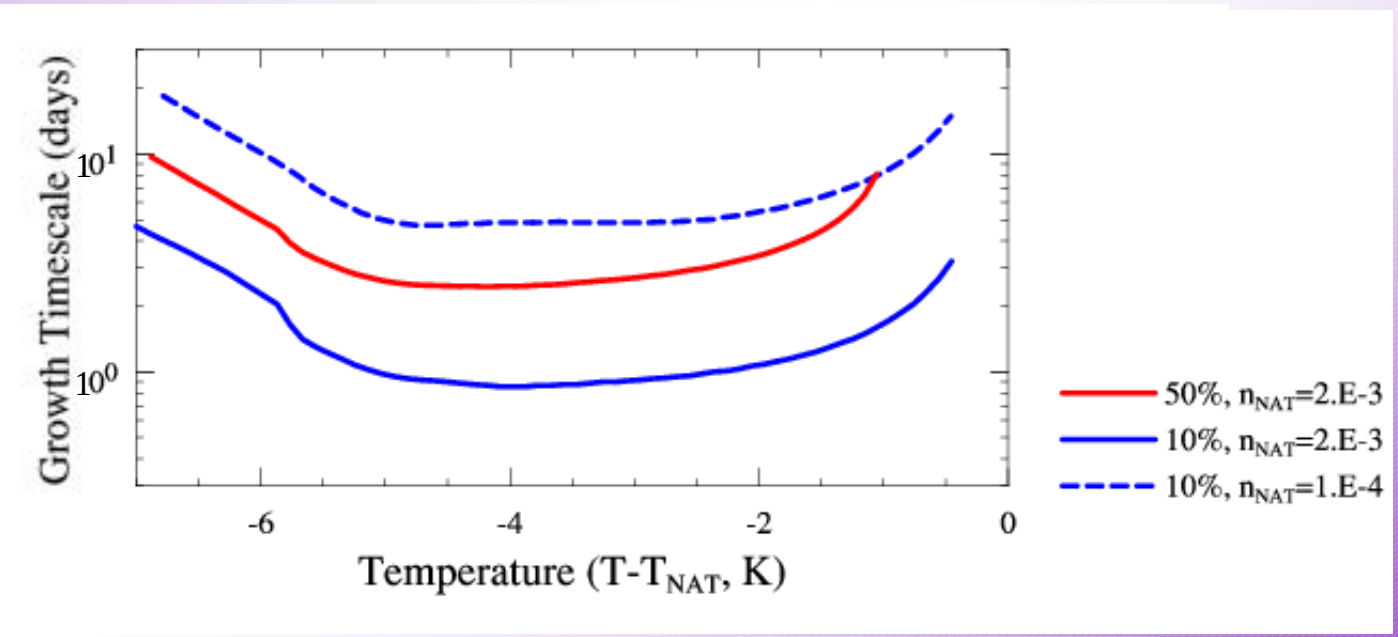
- Separating liquid and NAT components of measurements critical in analyzing PSC behavior
- Growth time scales must be taken into account to understand NAT characteristics

Model NAT growth rates

NAT growth has non-linear temperature dependence

"growth window" [McKinney et al., 2004]

Below T_{NAT}-5 K, liquids remove most HNO_3 from gas phase, severely limiting NAT growth



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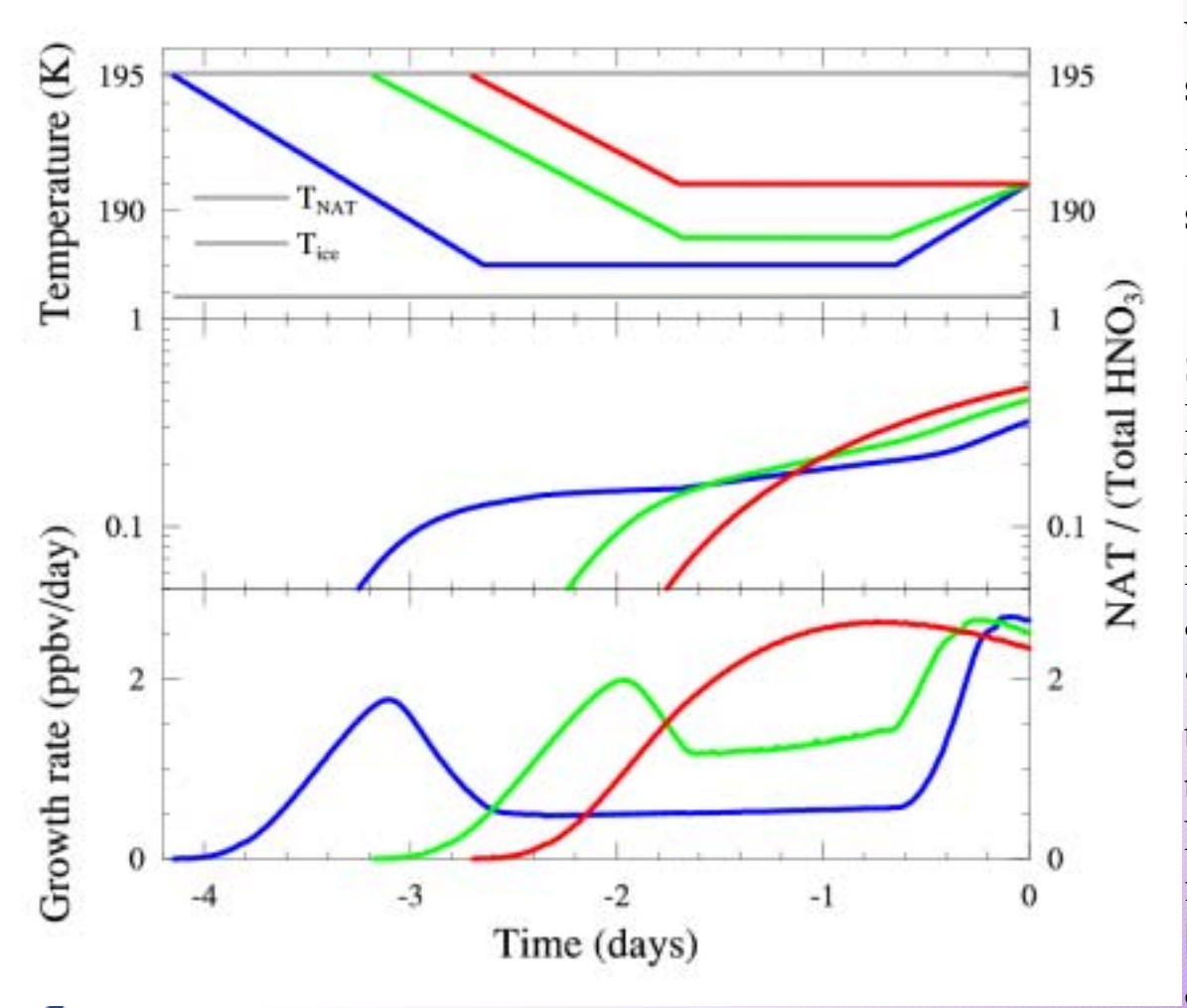
Implications for PSC characteristics



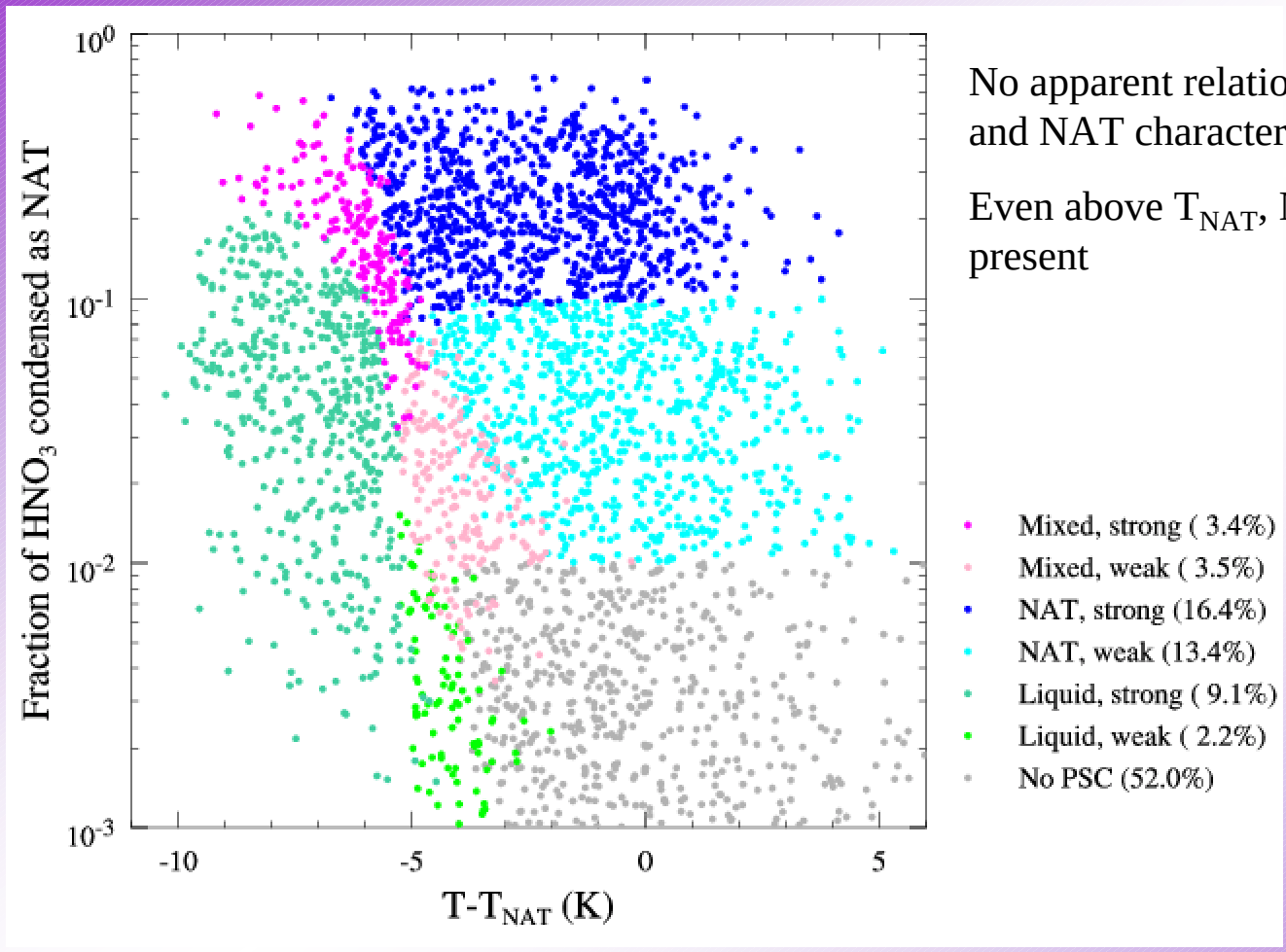
Warmest trajectory produces the strongest PSC!

In colder trajectories, growth slows down below T_{NAT}-5 K

Simple correlations between PSC extinction and temperature history (i.e., days below T_{NAT}, minimum temperature) should not exist. Explains results such as:

"We conclude from this study that factors, other than temperature and temperature history, are partially responsible for the formation of NAT PSCs" [Steele et al., 2002; regression analysis of 4 Antarctic winters of POAM data]

Model temperature correlations



No apparent relationship between temperature and NAT characteristics

Even above T_{NAT}, NAT continues to be present

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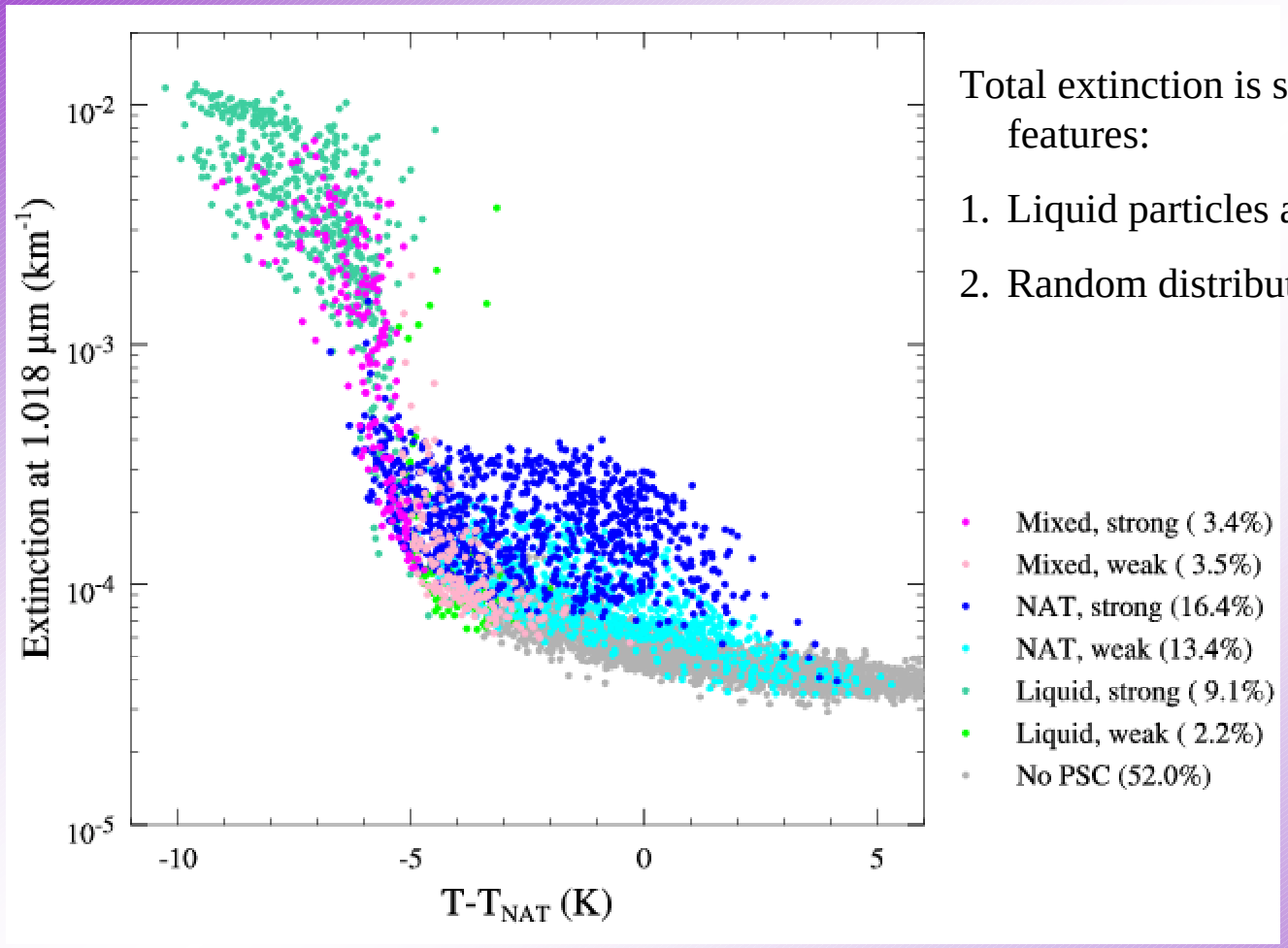
Model temperature vs. extinction



Total extinction is superposition of two features:

1. Liquid particles at equilibrium
2. Random distribution of NAT particles

Is temperature history useful?

Fundamentally, temperature is what determines PSC characteristics, so temperature history should provide information

Need to define PSC/temperature correlations that are specific to the question being asked. For example:

- Liquid PSCs should correlate with current temperature
- In testing PSC formation mechanisms, examine whether temperature has been below formation threshold
  - Can expect absence/presence of NAT PSCs to show a trend, but magnitude of extinction may show no correlation

What are the answers?

1. **What are PSCs made of?**

Mixture of liquid and NAT particles, with any possible ratio of liquid to NAT

2. **How do PSCs form?**

Multiple freezing mechanisms occur, any or all of which may influence a given PSC

3. **How do PSCs grow?**

NAT PSCs are never in equilibrium; growth is a complex function of temperature history

Implications for satellite measurements

1. **PSC 1a/1b discrimination techniques need to be fully characterized**
2. **Satellite measurements can provide answers on PSC formation, especially because of large-scale coverage. Maps of PSC concentration would be particularly useful in quantifying freezing rates.**
3. **Temperature/PSC correlations need to be defined that are specific to the question being examined**

Other issues….

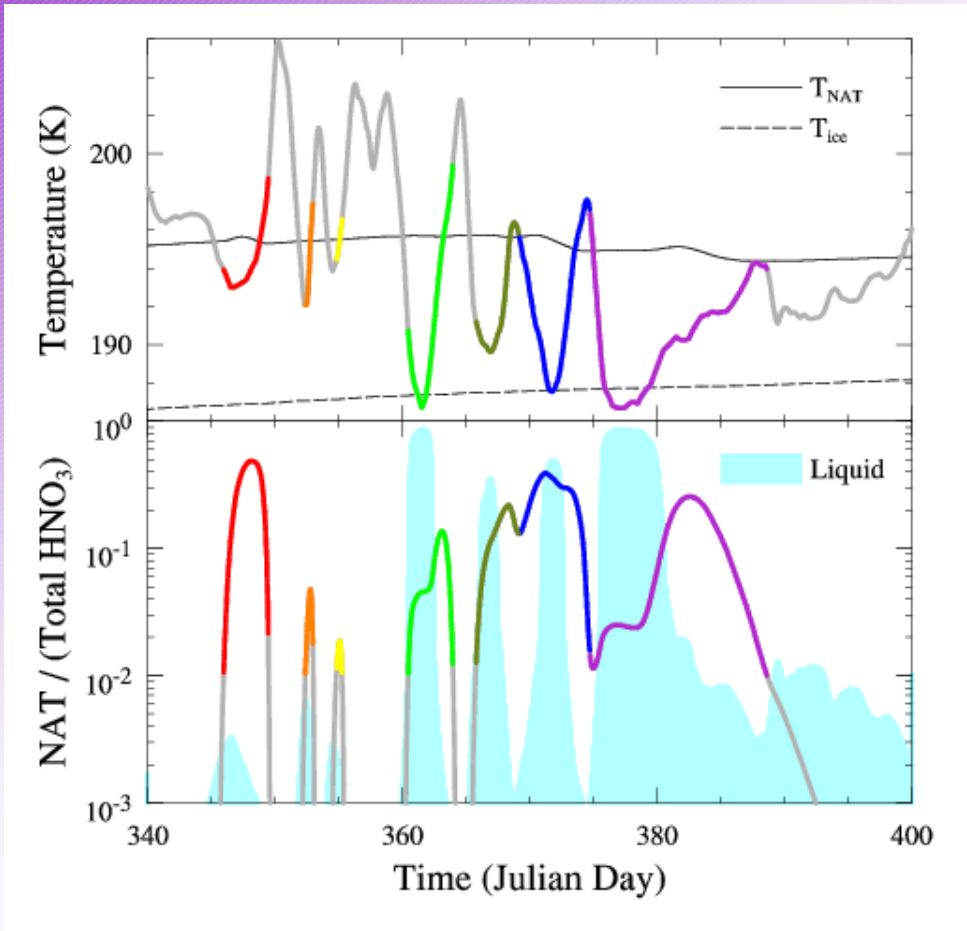
NAT particles are not spheres… effect on extinction?

Uncertainties in colocated temperature, HNO_3, and H_2O

Quantify effect of inhomogeneities, especially for NAT particles

Supplementary Material

Evolution of Sample Trajectory



How do PSCs evolve along a real trajectory?

Colors show where NAT is present (more than 1%); different colour used for each PSC event

First three PSCs: NAT growth, 1a PSCs

Remaining PSCs: Both NAT and liquid growth, vary between 1a and 1b

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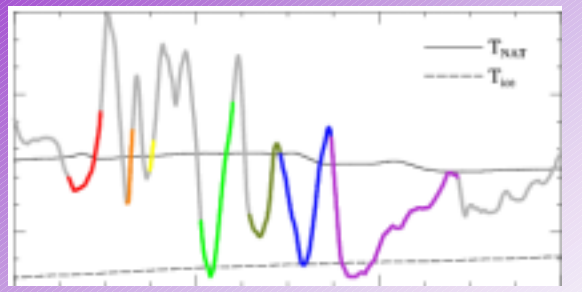
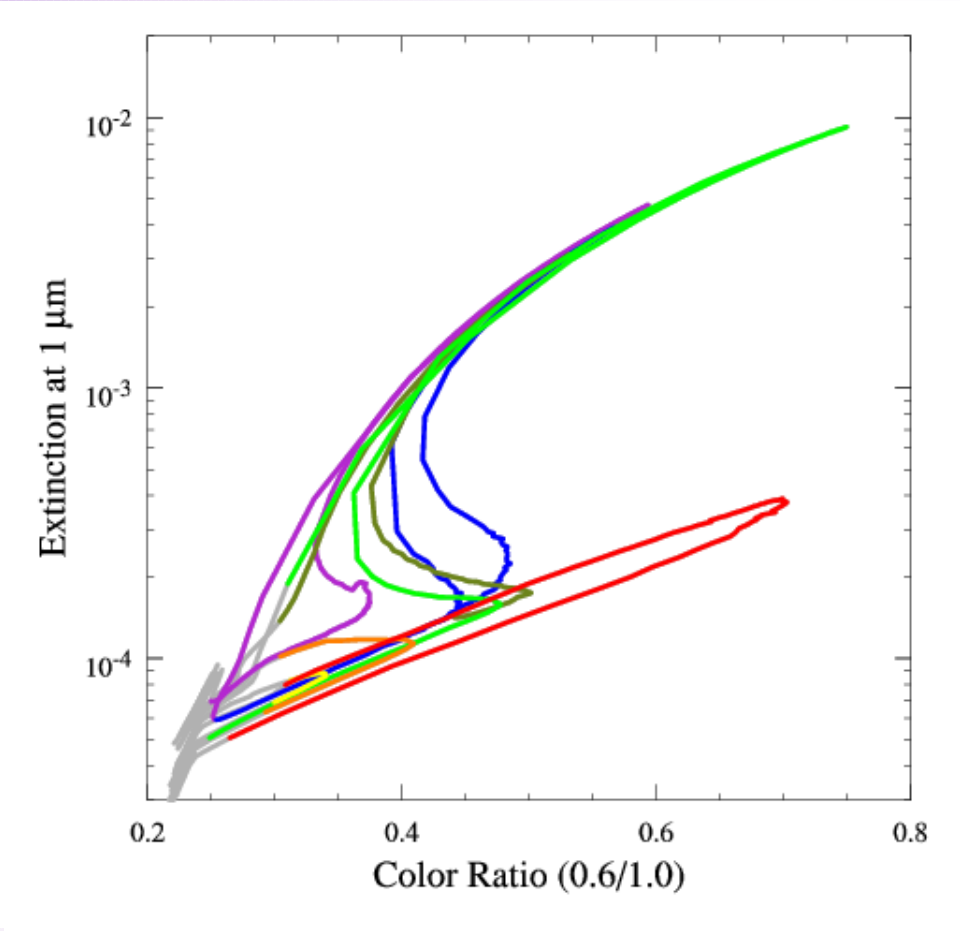
Extinction of Sample Trajectory



Each PSC event follows different path on extinction-color ratio plot



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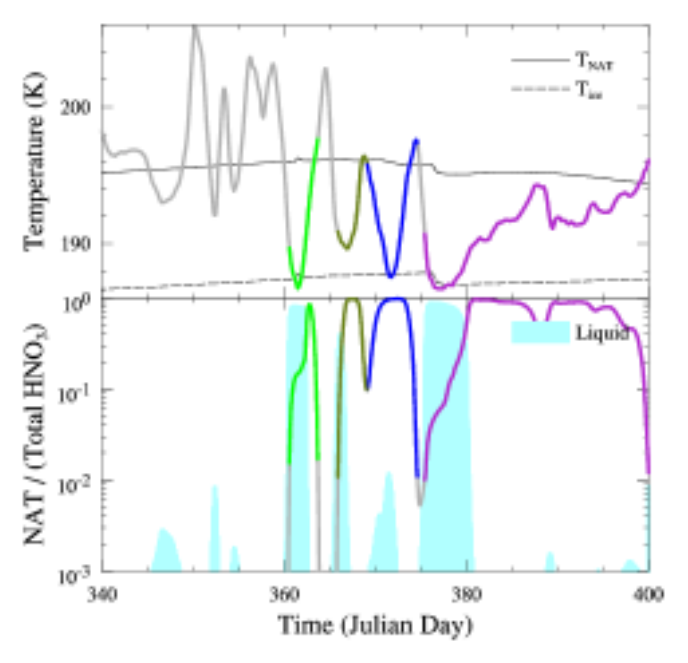
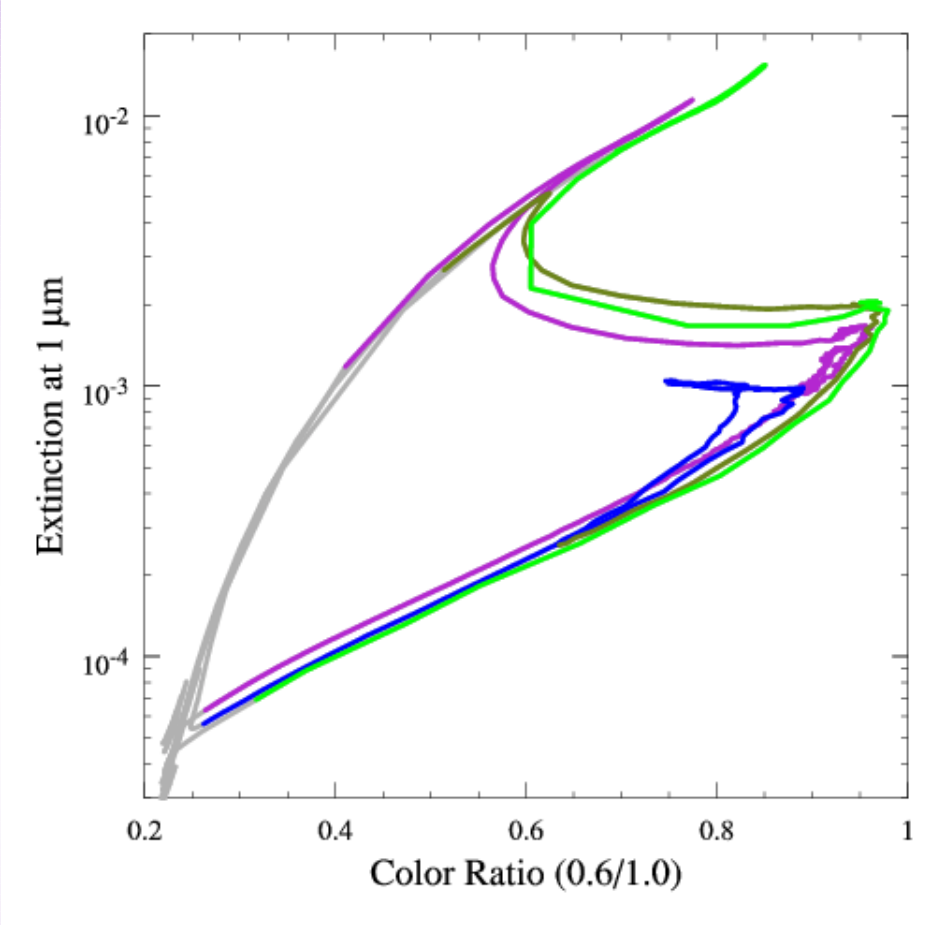
Sample trajectory – surface-based freezing

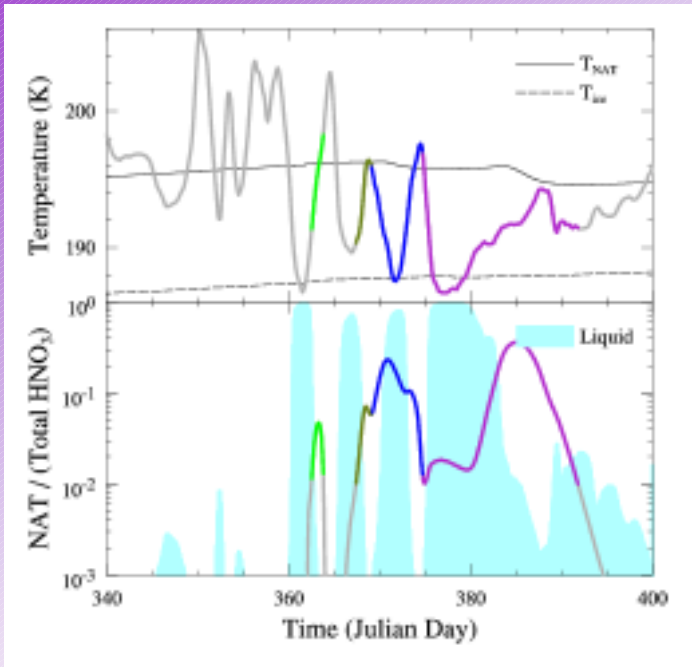


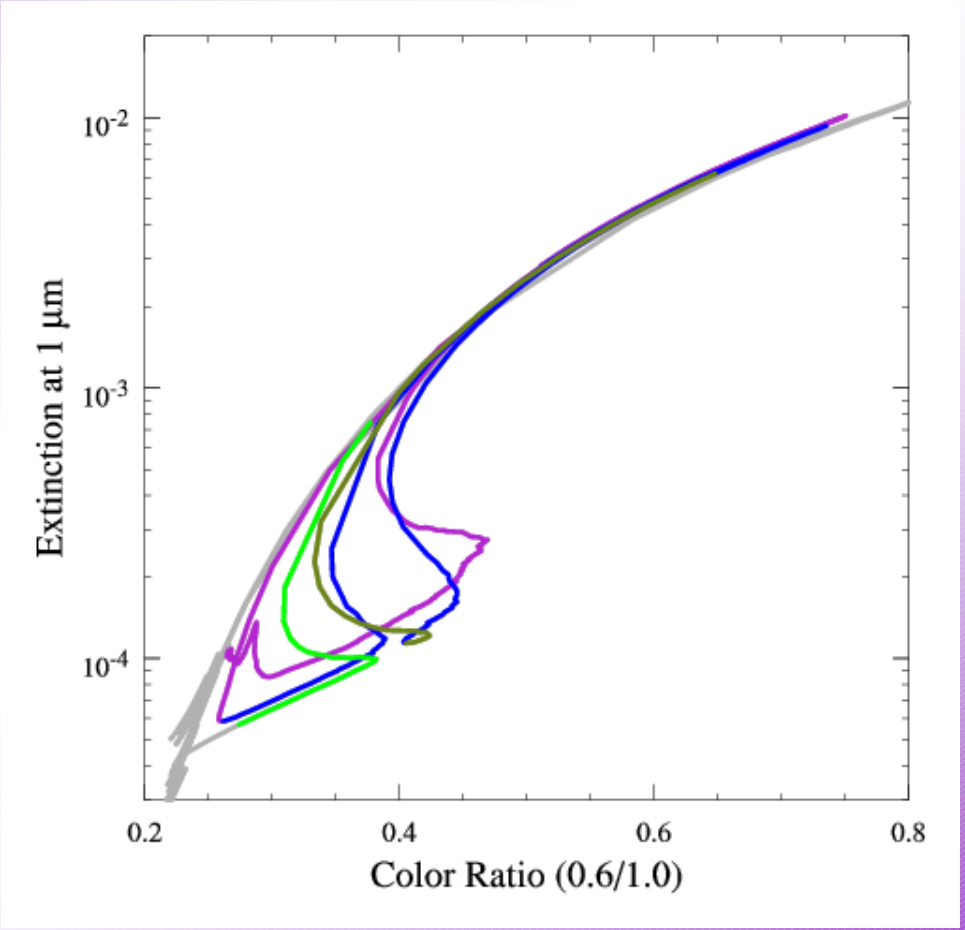


No NAT until after 1b formation

Very strong 1a events because of large NAT concentration

Sample trajectory – volume-based freezing

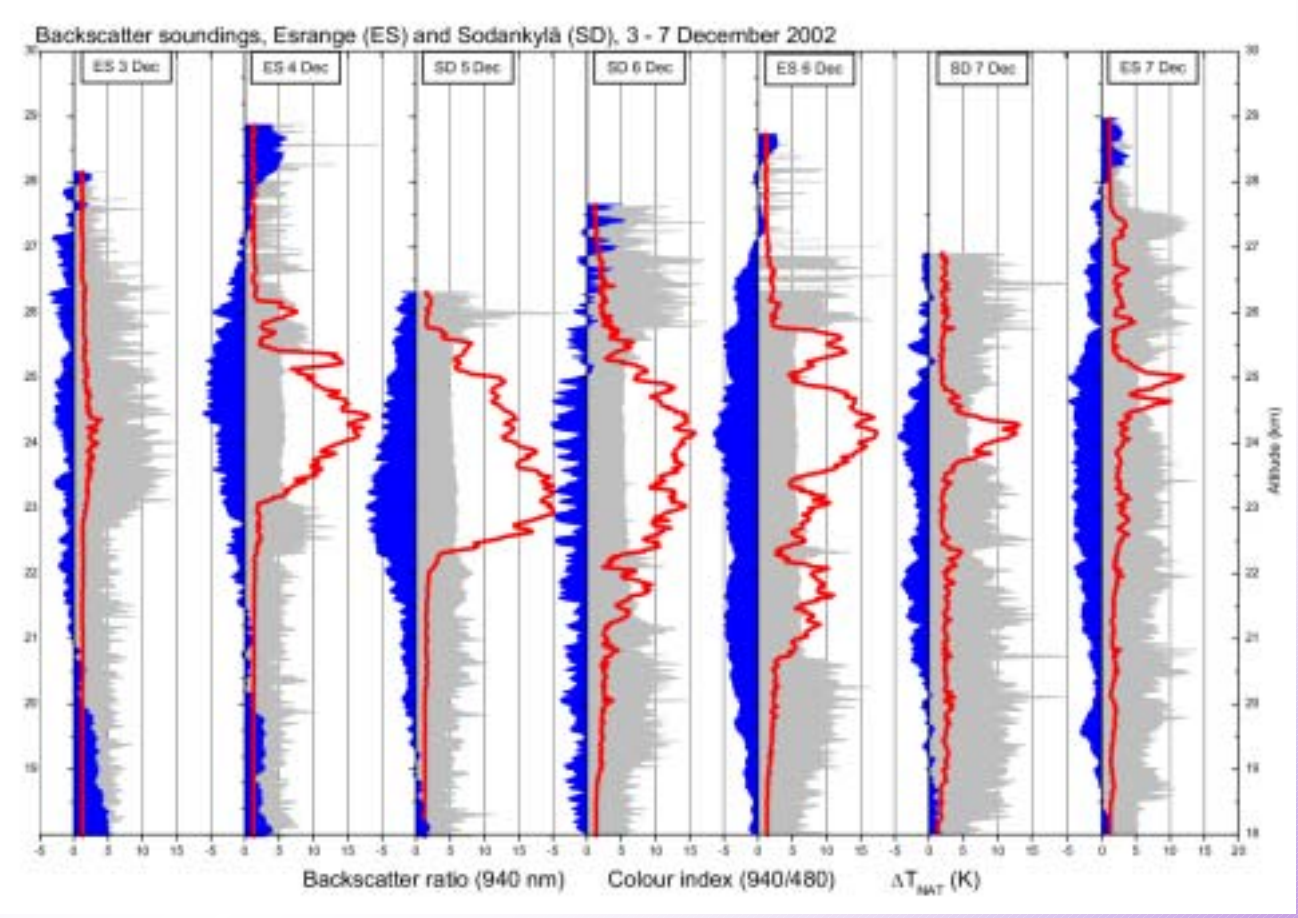




No NAT until after 1b formation

Weak 1a events because of small NAT concentration

Arctic PSC Profiles from December, 2002



- Type 1a PSCs whenever $T<T_{NAT}$ as early as Dec. 3
- Later profiles show "sandwich" structure with 1b PSCs at coldest temperatures

[Larsen et al., *ACPD* 2004]

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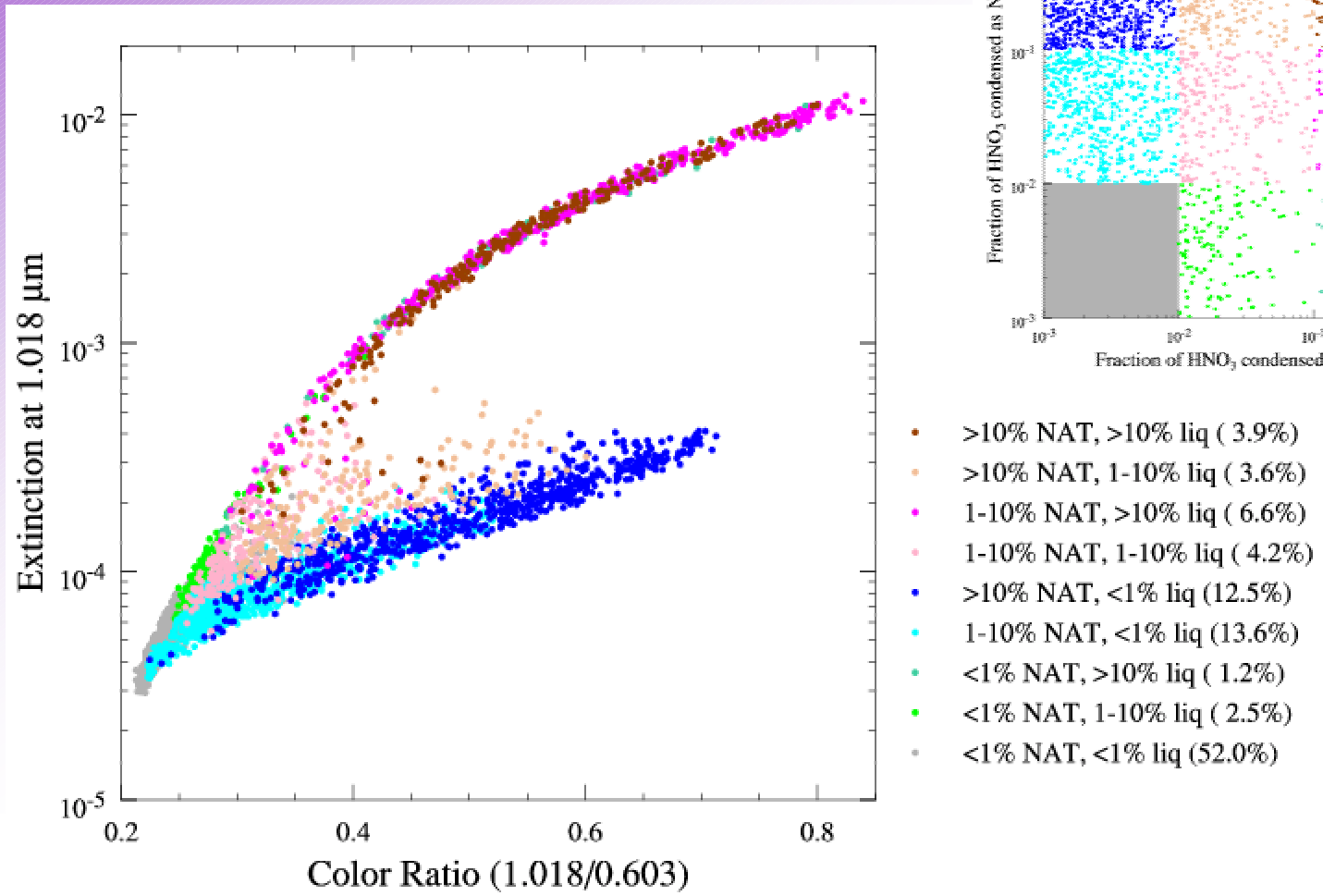
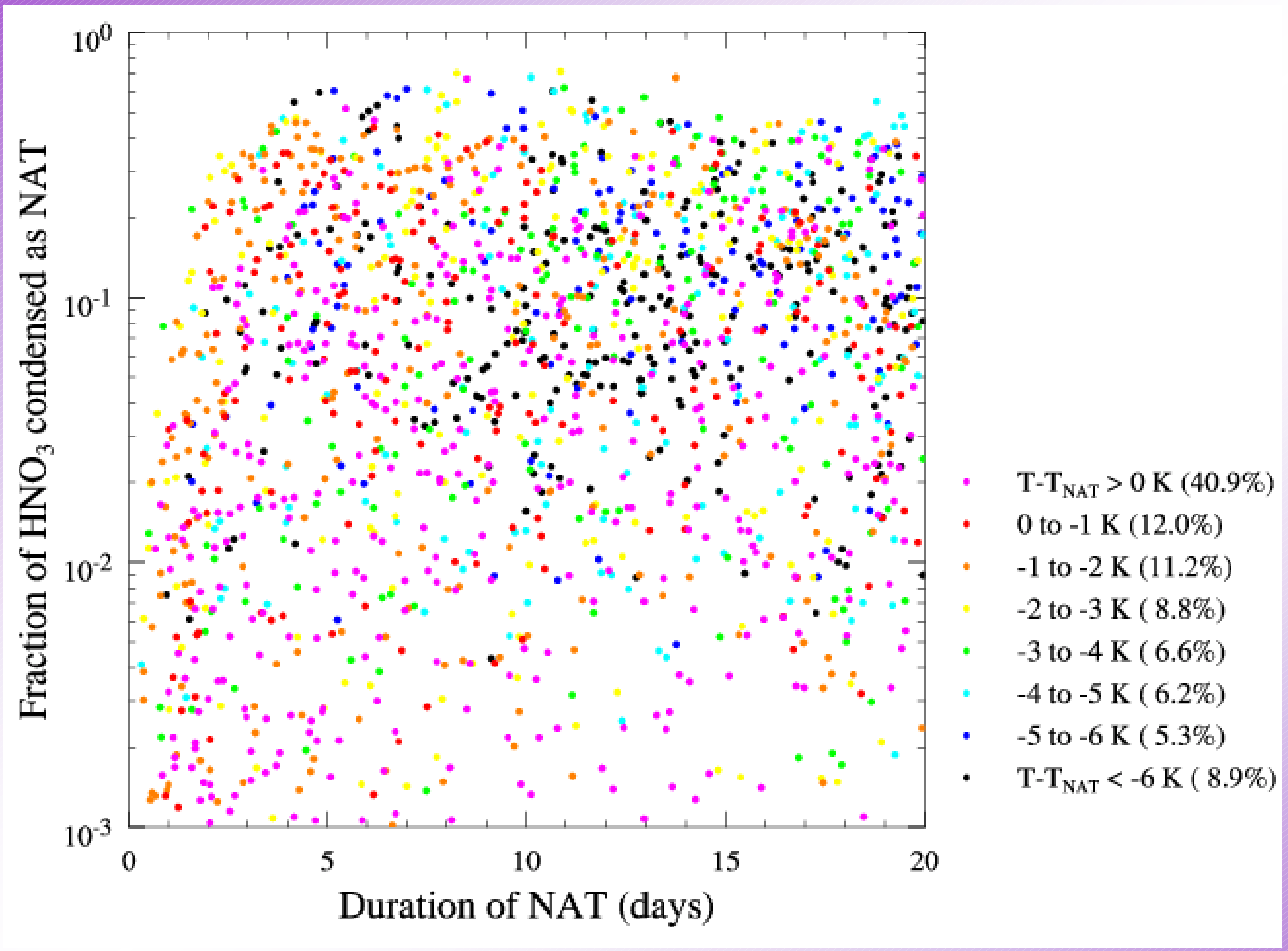
Alternative model PSC description



Model temperature correlations



Total time below T_{NAT} since start of winter
(NOT time in current cold pool)