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A-Train CALIOP and MLS Observations of Early Winter Antarctic Polar Stratospheric Clouds and Nitric Acid in 2008

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We thank the referees for their careful reading of the draft manuscript. We address their comments in the following text and plan on submitting a revised manuscript accordingly.

Referee #1

Lambert et al. present a careful and comprehensive study of PSCs in the Antarctic vortex based on remote sensing observations and modeling. The study integrates A-train measurements by AIRS, CALIOP, and MLS, and from MIPAS. These measurements provide information about the gas phase composition as well as particulate matter (derived from optical properties). In addition, meteorological data (temperature and winds) from GEOS-5 DAS is used to support thermodynamic arguments about cloud properties. This reviewer greatly appreciates the efforts undertaken to integrate this rich and diverse dataset to obtain a coherent description of the evolution of PSCs in the Antarctic vortex. Apart from the minor corrections/suggestions listed below, my main (and only) concern with this (long) study is that the reader (at least I did) loses the overview. I understand that, by virtue of being a comprehensive paper, presentation of the background information does require room. Nonetheless, I think the material could be probably streamlined and presented in an order that would make it more accessible. For example (a suggestions only), one could first briefly discuss the issues of PSCs only from a microphysical perspective. Then, one could discuss the optical properties, and possibilities and limitations to retrieve cloud microphysical parameters. This would then lead to the last step of integrating thermodynamic arguments (i.e. equilibrium modelling), and lastly, one could sketch how these aspects are integrated for this study. The discussion of the observations could then be done without replication of theory (and debates). For me, it remained difficult throughout the paper to keep the overview over 'what constrains what' - and, in essence, understanding how robust the conclusions are. For example, the thermodynamic equilibrium model calculations employed to constrain the information from the remote sensing measurements may not always valid. The manuscript mentions non-equilibrium effects in the context of fast processes, but it should be noted (and I haven't seen such a statement - perhaps I have overlooked it?) that the growth of NAT particles to sizes of several microns is also a non-equilibrium process, and the considerable fall distance (combined with wind shear) may make interpretation of co-located gas phase and particle measurements ambiguous. Having said this, I'd like to emphasise again that I appreciated the effort undertaken, and I am looking forward to seeing the revised manuscript.

We will address the issues raised with the presentation of the material and improve the flow of the discussion in Sections 2, 3, and 4.

Specific comments:

P29284/L21-24 (Abstract): *The sentence is ok, but difficult to understand.*

These lines will be rewritten:

The observed region of depleted HNO3 is substantially smaller than the region bounded by the NAT existence temperature threshold. Temperature-time histories of air parcels demonstrate that the depletion is more clearly correlated with prior exposure to temperatures a few kelvin above the frost-point.

P29284/L24ff (Abstract): *There is potential for confusion here; perhaps eliminate all non-essential information (e.g. reference to 2003).*

These lines will be rewritten:

From the combined data we infer the presence of large-size NAT particles with effective radii > 5–7μm and low NAT number densities $< 1 \times 10^{-3}\,\text{cm}^{-3}$. This denitrification event is observed close to the pole in the Antarctic vortex before synoptic temperatures first fall below the ice frost point and before the widespread occurrence of large-scale NAT PSCs. An episode of mountain wave activity detected by AIRS led to wave-ice formation in the rapid cooling phases over the Antarctic Peninsula and Ellsworth Mountains, seeding an outbreak of NAT PSCs that were detected by CALIOP and MIPAS. The NAT clouds formed at altitudes of 18–26 km in a polar freezing belt and appear to be composed of relatively small particles with estimated effective radii of around 1 μm and high NAT number densities > 0.2 cm^{-3}. This NAT outbreak is similar to an event previously reported from MIPAS observations in mid-June 2003.

P29291/L11-13: *Sentence not quite clear - my interpretation is that it says that the Hoepfner et al. observations do not require a 'NAT-freezing belt'; right? Please clarify.*

The stratospheric polar freezing belt (Tabazadeh et al., 2001) refers to a region of temperatures around the Antarctic continent lying within a temperature range above the ice frost point but below the NAT existence temperature (Tabazadeh et al., 2001) i.e. a zone conducive to the stability of NAT particles if they were to be nucleated somehow. We used the phrase 'NAT-freezing belt' in a couple of places, which might be taken to imply the actual existence of NAT particles in the belt, rather than the phrase 'polar freezing belt'.

Hoepfner et al. pointed out that although temperatures both upstream (westward) and downstream (eastward) of the Antarctic Peninsula were in the same range, only NAT-particles were observed forming downstream from the location of wave-ice induced heterogeneous nucleation. The presence of the 'polar freezing belt' is in fact necessary for the growth and stability of the NAT-particles downstream of the Peninsula following the wave-ice nucleation. However, in this case, a 'polar freezing belt' alone was not a sufficient condition to form similar NAT-particles in the region upstream of the Peninsula.

These lines will be rewritten:

L1-3: However, other work has highlighted the role of mountain wave events over the Antarctic Peninsula in triggering heterogeneous nucleation of NAT on ice and explaining the formation of a circumpolar belt of NAT PSCs observed by satellite measurements.

L11-13: They observed a sudden onset of NAT PSCs over a few days from 10–12 June 2003 in a region downstream of the Antarctic Peninsula within a polar freezing belt (Tabazadeh et al. 2001), but they noticed the absence of PSCs within the belt in the region upstream of the Peninsula despite similarly low synoptic temperatures.

P29299/L25ff/Figure 1: *I have difficulties seeing the importance of Figure 1.*

We prefer to retain Fig 1 in the paper since it provides an overview for the reader who may not be familiar with the high density of the spatial and temporal coverage of the CALIOP and MLS instruments over Antarctica. It also provides an approximate pressure-altitude conversion. An arrow showing the progression of the orbits in time was omitted from the submitted draft figure and will be included in the revision.

P29304/L1: *I would think that the particle shape (or lack of knowledge thereof) is a problem, and a word about uncertainties would be helpful here.*

Particle shapes are likely to be physically more complex figures than spheroids or cylinders, however these are commonly used for the interpretation of lidar measurements.

The degree of non-sphericity is defined by the particle aspect ratio, e, and we used the definition given in the T-matrix code of Mishchenko and Travis (1998), $e = a/b$, where a is the horizontal semiaxis and b is the rotation (vertical) semiaxis. Therefore, $e < 1$ represents prolate shapes and $e > 1$ represents oblate shapes. Often in the literature the aspect ratio of prolate spheroids is quoted as a value greater than unity, i.e. as the reciprocal of e.

The CALIOP PSC classification regions determined by Pitts et al. (2009) are based on T-matrix calculations assuming NAT particles to be oblate spheroids with $e = 1.2$, although no reference is given in their paper for this particular value.

Two papers we referenced and a preliminary study we performed but did not discuss provide the justification for our choice of spheroidal aspect ratios.

- Liu and Mishchenko (2001) indicated that lidar measurements of Type Ia PSC particles could be explained by:
  - spheroids (oblate or prolate) with aspect ratios larger than 1.2, i.e. $e > 1.2$ or $e < 0.8$
  - oblate cylinders with diameter-to-length ratios larger than 1.6 and prolate cylinders with length-to-diameter ratios larger than 1.4
- Toon et al. (1990) cite a paper by Taesler et al. (Acta Crystallogr, Sect B, 31, 1489-1495, 1975) which reported that trihydrate crystals grown from liquid were cylinders with length-to-diameter ratios of about 1.22. Toon et al. approximated this cylindrical shape with a prolate spheroidal aspect ratio (using the Mishchenko and Travis definition here) of $e = 1/1.22 = 0.8$.

- We explored the uncertainties in particle shape within the limits of computation for the T-matrix spheroidal model by performing calculations (not discussed in the paper) for monodisperse 1-micron and 6-micron radius NAT particles with aspect ratios from 0.7 to 1.5 in 0.025 increments. For the 6-micron radius particles we found a plateau in the depolarization ratio (around $10 \pm 5\%$) in the prolate range $e = 0.70$–0.85 and a higher plateau (around $25 \pm 5\%$) in the oblate range $e = 1.2$–1.5. The more nearly spherical particles ($e = 0.90$–1.10) show substantially larger depolarizations (over 60 %). A similar effect for spheroidal aspect ratios near unity and increasing particle radius was noted by Liu and Mishchenko (2001), who also commented that backscatter characteristics are more aspect-ratio dependent for spheroids than for cylinders.

- We therefore used two spheroidal aspect ratios in the depolarization plateau regions determined above (prolate, $e = 0.8$ and the "reference" CALIOP oblate, $e = 1.2$) to illustrate the range of the sensitivity of the perpendicular backscatter coefficient as indicated in the text at P29307/L3 and in Fig4(d).

Also of relevance to the question of uncertainties in particle shape are the following two papers:

- Brooks et al. (Polar stratospheric clouds during SOLVE/THESEO: Comparison of lidar observations with in situ measurements, J. Geophys. Res., 109, D02212, 2004) used data from in situ measurements on the ER-2 (Multiangle Aerosol Spectrometer Probe, MASP, and Focused Cavity Aerosol Spectrometer, FCAS III) to calculate aerosol backscatter and depolarization ratio at visible (632nm) and infrared (1064nm) wavelengths and compare with lidar measurements on the DC-8 and Falcon aircraft during 2000 SOLVE/THESEO. In the presence of large particles (r > 5 μm) the best fit was obtained for a refractive index 1.3–1.6 and an aspect ratio of 1.5–2.0. We assume that Brooks et al. meant these to be interpreted as oblate aspect ratios since they also use the Mishchenko and Travis T-matrix code and the phrase "horizontal to vertical aspect ratio (A/B)" in their figure captions. However, on the one occasion where they mention prolate or oblate in the text, they appear to have inadvertently reversed the sense on Page7:Line 1, since they quote "for prolate and oblate spheroids of aspect ratios 2 and 0.5, respectively", which we believe to be a typographical error.

- Wagner et al. (Infrared Spectrum of Nitric Acid Dihydrate: Influence of Particle Shape, J.Phys. Chem., A. 109, 2572–2581, 2005) concluded from comparisons of T-matrix calculations with infrared spectral measurements of laboratory generated homogeneously nucleated NAD crystals with median radii of ≤ 1 μm that their shapes were predominantly oblate. Since their nucleation experiments mimicked a potential pathway for the formation of nitric acid hydrates in the atmosphere, they inferred that PSCs could be composed of highly aspherical and possibly platelike particles (i.e. oblate $e > 5$). These large aspect ratios are outside the range investigated for the atmosphere by Liu and Mishchenko (2001), and by Brooks et al. (2004).

We will add a description of the rationale for the choice of the aspect ratio and add references to Taesler et al. (1975), Brooks et al. (2004) and Wagner et al. (2005).

P29306/L20ff: *This is one of several instances where it was not clear to me what is constrained by observations, and what by model calculations, and whether the model calculations* *assume thermodynamic equilibrium; and if so, whether this would not conflict with a size of 6 micron (radius), which requires a long period of non-equilibrium conditions to grow to this size. And, lastly, whether the fall distance of the particle during growth is not similar, or even greater, than the 'cloud thickness', such that the local conditions (gas phase) at the position where the cloud is observed may not provide information about the cloud itself.*

In the first part of this section we compare the theoretical limits of the detection of PSCs and HNO3 depletion based on the modeled properties of liquid-solid PSC mixtures and T-matrix calculations. Two cases are presented relating to small particle size/large number density and large particle size/small number density PSCs, which are relevant for observational scenarios concerning NAT formation through slow and fast cooling.

- The microphysical/optical model calculations outlined on P29303 follow the methodology of Pitts et al. (2009) and do not assume that the NAT particles are in equilibrium.
- A range NAT particle sizes (effective radii) and number densities are modeled but the resulting NAT volume is constrained to not exceed the available equilibrium NAT volume (noted on P29303/L22). The equilibrium volume curves for NAT are shown for comparison in Fig 4 as dashed lines. In this model NAT-particles cannot be larger than their equilibrium size.
- Thermodynamic equilibrium is assumed for the STS particles after allowing for the amount of HNO3 condensed in the NAT particles (P29303/L22-25). This is in general a good approximation for STS (e.g. Drdla et al., 2003).

In the second part of this section we develop a method to provide coarse separation of PSC clouds into small particle or large particle categories from a model fit to the data.

- The HNO3 uptake adds a useful independent measurement to the lidar backscatter properties and provides more information to allow the selection of a particle size / number density combination by a minimization search of Eqn (6) than if it were based on the total and perpendicular backscatter measurements alone.

We apply the method to observations in Section 4.

- For the two case studies we consider: (a) P29313/L1 and (b) P29317/L23 we are able to estimate the initial total HNO3 at about 14 ppbv, from the MLS data taken at earlier observation times before uptake into the PSCs.
- Certainly the distribution of the HNO3 field reflects a time-integrated process and, as has been noted, the gas phase HNO3 alone does not provide sufficient information about the local conditions for the PSC clouds. We state that in general there is a problem in estimating the total ambient HNO3 (P29307/L18-20).
- The fall distance of a 5 micron diameter particle is 4 km in 4 days (P29312/L17). Although the PSCs and HNO3 field are developing over this time, we are not attempting to model the time history here with a PSC growth model. We use the co-located observations (within 30 secs and 2 km horizontally) to provide vertical atmospheric profiles at

a particular time. The total ambient HNO3 is the sum of the gas phase HNO3 and the HNO3 contained in condensed form in the NAT and STS particles. The MLS gas phase HNO3 combined with an estimated total ambient HNO3 at the PSC location provides the gas phase fraction coordinate in Eqn (6).

- For case (a): the total HNO3 will have been been reduced from the initial value over time by loss from sedimentation of large NAT particles. If we equate the HNO3 "excess" in the renitrified area, which contains about 2 ppbv, to the amount lost by sedimentation then we can approximate better the total HNO3 at the height of the PSC at the measurement time as about $(14 - 2) = 12$ ppbv. Therefore, since MLS measures 7 ppbv of gas phase HNO3 at the PSC location, we can estimate the gas phase fraction to be about $7/12$ or $58\ \%$. This correction results in revised values of effective radius close to $r_e = 7\ \mu$m and $N = 0.001$ cm^{-3}, which were obtained for the uncorrected gas phase fraction of $7/14$ or 50% (P2913/L1). Note that the values of $r_e > 7\ \mu$m were not simulated for the microphysical/optical model and the Eqn (6) fit is returning practically the largest radius available. However, it is clear that small particles are not a good fit for this case.

- For case (b): sedimentation of the PSC particles in the NAT outbreak is not an issue over the time range of the observations as the sizes are small (of the order of 1 μm or less) for the wave-ICE and NAT. Therefore no loss of initial total HNO3 by sedimentation is expected and no correction for the total ambient HNO3 at the PSC location is required.

- Note that we are not claiming to be able to provide precise sizing information from minimization of Eqn (6), but we conclude that cases (a) and (b) demonstrate that a broad categorization of PSCs into small particle/large number density and large particle/small number density can be achieved. Fig 4 can be used graphically to check the differences expected for these two scenarios.

P29314/L12ff: *This is an example where the paper is unnecessarily hard to read, as the paragraph combines information that does not belong together. Perhaps the information about H2O could be given first (page 29310)?*

We will move the reference to the lack of significant dehydration during the denitrification event, although it seems a relevant point on which to end the section rather than to place it at the start.

Referee #2

This study primarily combines CALIOP and MLS observations to examine PSC formation and the resultant denitrification in the Antarctic and clearly demonstrates the power of combining observations from multiple instruments to gain a better quantitative understanding of the processes examined. This work is extremely thorough and the analysis which also includes examination of data from other satellite instruments and the use of a range of models is exceptional. The introductory sections (Section 1 and 2) also clearly demonstrate the expertise and understanding of the authors and more than provided the relevant background for the reader. I also found Section 4.5 particularly valuable and it would be well worth a paper in its own right in my opinion. The authors should be proud of the work that they have completed. The very complete and high quality of the analysis performed in this work means it is clearly worthy of *publication. I have indicated a very small number of suggestions for improvement considering the length of the paper below.*

Suggestions/Questions

Organisation: *The work in Section 3 and 4 is very detailed and some areas would be improved by adding some extra explanation and/or providing summaries of the main points at the end of certain sections. For example, Section 4.4 and 4.5 are both quite long and summarising the main findings as bullet points at the end of these sections would probably help the reader as the text is very dense and the length of the work means important points can be easily missed.*

We will incorporate these suggestions in the revised manuscript.

Page 29298 Line 5: *Is this under an assumption of Rayleigh scatter?*

Although this is commonly referred to as Rayleigh scattering, CALIOP detects only the the narrow Cabannes region. The volume molecular backscatter coefficient used in Eqn (3) and the molecular depolarization value Eqn (5) depend on the receiver filter bandwidth. For the CALIOP narrow bandwidth optical filters, only the central Cabannes line of the Raleigh backscatter signal is detected and the full details of the calculations used are given by Hostetler et al. (2006).

Page 29298 Line 20: *Are these equations really necessary they seem obvious.*

These additions were requested by the editor.

Page 29304 Sentence starting on Line 1: *Do you mean you simulated with two aspect ratios or in a range between the two limits? Some extra explanation of this point would be useful.*

Only a single aspect ratio value of 1.2 is used for the microphysical/optical model used for the CALIOP PSC classification (Pitts et al. 2009). We will change the text at this point to make it clear. An additional value of 0.8 has been used in this paper to illustrate the sensitivity of the perpendicular backscatter coefficient as indicated in the text P29307/L3 and in Fig4(d). Please see also the response to Referee #1.

Page 29310: *I think the TTE idea and correspondence between high TTE areas and denitrification is excellent, perhaps this deserves extra emphasis in the Conclusion section.*

We will add a statement in the conclusions.

Page 29317 Line 4: *I may have missed something earlier. But, can you clarify where the renitrification occurs exactly along the track and why it is renitrification rather than an area which has never been denitrified.*

We have determined that renitrification occurs because the values of HNO3 in Fig14(f) located at along track coordinate -500 km and at a height of 15 km exceed the maximum HNO3 values seen at the same height prior to the onset of denitrification. Therefore we assume that this occurs via the sedimentation and evaporation of NAT PSCs. Observations of MLS O3 remain fairly constant at the same level and also indicate this is not the result of diabatic descent. The renitrified area extends below the height of NAT existence temperature contour shown in Fig14(h) indicating the likelihood of eventual evaporation of NAT particles which descend into this warmer region. We will add this clarification to the revised manuscript.

Page 29319 Sentence starting on Line 18: *Given the mean background wind field wouldn't it be surprising if the trajectories didn't pass over the peninsula? Therefore can you prove this point in another way?*

Agreed. The back trajectories passing over the Peninsula are not at all surprising given the circumpolar flow. However, we should have indicated more clearly in the text that we have also demonstrated a time correlation. In addition to the location of the passage of the trajectories in Fig 16(d) over the Peninsula, their earliest passage was coincident with the start of the gravity wave activity and first wave-ice detection by MIPAS on 28 May. Please see also the response to the question concerning Fig 16. We will add this clarification to the revised manuscript.

Figure 7 and 14: *Can you add scales to (h) so that you remove (g) and (i) in these figures?*

In this case we would have to move (j) from the rhs vertical column (b,e,f,h,j) and place to the lhs of (h). Color codings in 7(i) and 14(i) are used to indicate the along-track locations in Figs 8 and 15, respectively. These will be added to the new scales under (j) and (h).

Figure 16: *Either the caption or panel(c) needs improvement as I can't understand the colorlabel.*

This is the same kind of plot as used for MIPAS in Fig 11(d). We will rewrite the captions. The color scale relates to both the PSC observation times (bold line segments radiating axially from the center of the plot) and the location times of air masses calculated along the trajectories. Therefore, trajectories which pass near or intersect with PSC observations at coincident times have the same color.

Typographical suggestions

Page 29291 Sentence starting on Line 23: *This sentence is slightly confusing please clarify.*

These lines will be rewritten:

Denitrification has been observed without accompanying significant dehydration in both polar regions,. . .

Page 29295 Line 21: *Remove (hectopascal) this is not necessary.*

This addition was requested by the editor.