Author response to Reviewer #1 comments

We sincerely thank the reviewer for the valuable comments. Based on these we have made careful revisions and we believe that this has helped to improve the manuscript. Our point-by-point response to the review comments are given below. The comments are marked in bold blue font and our responses are marked in normal black font below each comment.

Reviewer #1

This is an ambitious paper with three goals, to show: 1) that the Australian wildfires of 2019 and early 2020 changed the character of the stratospheric aerosol incorporated into the 2020 austral polar vortex. 2) that these aerosol subsequently led to an enhanced abundance of PSCs, and 3) that a new analysis of pairs of CALIOPI observations, of related spatial locations south of 80 degrees, from different orbits of the instrument, can be used to make conclusions about PSC formation pathways.

There is some interesting analysis preformed in support of these goals, but ultimately the authors struggle to carry through with enough detail on any one of these topics to make a convincing argument. This deficiency increases as the paper moves through these three goals. The paper style is to describe each observational product with a short cursory analysis, reference and discussion of supporting literature, and then how this observation leads to the next issue to be tackled. A more normal style is to present a complete discussion of the background literature on the topics to be discussed, e.g. stratospheric aerosol and PSCs, in the introduction, not to scatter such presentations throughout the rest of the paper. Once the literature is reviewed then it doesn't need to be continually re-cited. It will be obvious to the reader how the new analysis fits into the literature that was already reviewed in the introduction.

Thank you for the summary comments, the appreciation of the work and the valuable suggestions. As suggested, we moved supporting literature which were included in discussion sections to introduction section. Following the introduction section (Sect. 1, L35, page no, 2), we briefly review the current understanding about stratospheric aerosols and polar stratospheric clouds in newly added Sect. 2 (from L72 in page no. 3 to L131 4). In Sect. 2, we discussed the PSC types, composition, and types of formation pathways for ice and liquid-NAT mixture.

The paper cannot be accepted in its present form. Perhaps a paper tackling the first, or first and second, goals, and doing a complete job on that, has a possibility of acceptance. The third goal contains the germ of an interesting analysis idea, but requires significantly more work, much less generalization, and the need to ground any conclusions with a solid microphysical analysis. It is also incumbent for the authors to use the language of the PSC community and really reflective of the CALIOPI observations. Their current analysis is way too simplistic.

Thank you for the detailed comment. We understand the concern regarding our methodology to retrieve the formation pathways as it is highly generalizing (i.e., 300 km of radius at intersection points of CALIPSO scan track and reclassifying the PSCs into the most dominating type). To address this issue, we implemented major revision to the methodology to study the PSC formation pathways and improved the discussion and conclusion section thereafter, the gist of which is given below.

In this revised manuscript, to gain information about formation pathways of PSCs, instead of considering the intersection point of two CALIPSO scan track, we have examined the temperature history of the air parcels containing ice/liquid-NAT mixture through Lagrangian backward trajectory analysis along with corresponding changes in MLS HNO_3, and H_2O mixing ratio. Furthermore, as per the reviewer's suggestion, we fed these trajectories to the CLaMS microphysical box model, to simulate the PSC evolution and subsequent uptake of HNO_3, and H_2O and validated it against the MLS observed uptakes of these gases.

In addition, as suggested, instead of showing the results as average for the whole year and statistical analysis, in this revised manuscript, we presented results in the form of case studies along with results from CLaMS box model simulation. Totally 7 case studies have been added as described below:

- Liquid-NAT mixture formation pathways: 2 cases discussing ice-free NAT formation pathway (Case no. 1 in page no. 19 and Case no. 2 in page no. 22) and 2 cases discussing ice-assisted NAT formation pathway (Case no. 3 in page no. 24 and Case no. 4 in page no. 26).
- Ice formation pathways: 2 cases discussing NAT-assisted ice formation pathway (Case no. 5 in page no. 31 and Case no. 6 in page no. 32) and 1 case discussing NAT-free formation pathway (Case no. 7 in page no. 33).

The revised methodology is similar to Nakajima et al., (2016) and Voigt et al., (2018) who have studied the PSC formation pathways through investigating temperature history and CALPSO observed PSC type along the backward trajectories. We brief the methodology here below.

1. First, we choose the ice and liquid-NAT mixture PSCs from CALIPSO observation.

2. For these chosen PSCs, we calculated 48 h backward trajectories using CLaMS trajectories model and hourly ERA5 operational analysis meteorological data. The rationale behind choosing the '48 h' is that once the air parcel's temperature drops below T_{NAT} and following the nucleation of NAT particles with a number density of 5×10^{-4} and 5×10^{-5} cm^{-3}, within ~19 h (0.8 day) the NAT particles' perpendicular backscatter exceeds CALIPSO detection threshold and becomes detectable (Lambert et al., 2012). Similarly, Voigt et al. (2005) provided observational evidence from aircraft campaigns showing NAT formation within approximately 20 hours after the temperature drops below T_{NAT}. In the case of ice formation, the 48 h period also should be sufficient (considering the average cooling rate of the stratosphere). To support for choosing 48 h, in this present study, we also provided observational evidence of formation of liquid-NAT mixture and ice PSC within the 48 h once the temperature decreased below T_{NAT}.

3. To determine PSC composition along each trajectory, we identify intersection points where the backward trajectory crosses the CALIPSO scan track within a ±30-minute window i.e., at the intersection points, both trajectory and CALIPSO profile time should be within ±30-minute window. At each valid intersection, the PSC composition is assigned from the CALIPSO profile with the closest potential temperature to the trajectory point. In addition, the MLS observed gas-phase HNO_3, and H_2O are filled along the trajectory at the time of observation of PSC from CALIPSO. This creates the comprehensive

picture about temporal evolution of air parcel which leads to formation of ice/liquid-NAT mixture and help us to understand their formation pathways.

By carefully analysing backward trajectories of air parcels containing ice and liquid-NAT mixture PSCs, we retrieved their formation pathways, and relative percentage contribution of formation pathways for liquid-NAT mixture are estimated and given in Fig. 13 (c) (Sect. 4.54 in page no. 29 in the revised manuscript), and for ice given in Fig. 19 (Sect. 4.5.10 in page no. 37 in the revised manuscript).

We also validated the MLS observed uptake in HNO_3, and H_2O against the CLaMS modelled uptake in these gases during formation of ice and liquid-NAT mixture.

These are incorporated in the revised manuscript, with the specific cases on pages pointed out above.

Reference:

Lambert, A., Santee, M. L., Wu, D. L., and Chae, J. H.: A-train CALIOP and MLS observations of early winter Antarctic polar stratospheric clouds and nitric acid in 2008, Atmos Chem Phys, 12, 2899–2931, https://doi.org/10.5194/ACP-12-2899-2012, 2012.

Nakajima, H., Wohltmann, I., Wegner, T., Takeda, M., Pitts, M. C., Poole, L. R., Lehmann, R., Santee, M. L., and Rex, M.: Polar stratospheric cloud evolution and chlorine activation measured by CALIPSO and MLS, and modeled by ATLAS, Atmos Chem Phys, 16, 3311–3325, https://doi.org/10.5194/ACP-16-3311-2016, 2016.

Voigt, C., Dörnbrack, A., Wirth, M., Groß, S. M., Pitts, M. C., Poole, L. R., Baumann, R., Ehard, B., Sinnhuber, B. M., Woiwode, W., and Oelhaf, H.: Widespread polar stratospheric ice clouds in the 2015-2016 Arctic winter - Implications for ice nucleation, Atmos Chem Phys, 18, 15623–15641, https://doi.org/10.5194/ACP-18-15623-2018, 2018.

Here follow comments by line number initially tailored to help the authors with a better presentation, but then they evolved into questions/complaints/suggestions concerning the authors increasingly inability to present a complete picture and thorough analysis of a topic before moving on. Quotes from the paper are bracketed with ellipses.

24, 83 LNAT – This acronym is misleading. It suggests a liquid NAT particle which doesn't exist. Stick with the nomenclature of Pitts et al., e.g. liquid-NAT mixtures. Then there is no confusion. Upon reading the abstract and seeing this acronym I was prepared to read a paper not conversant with the PSC literature or expecting to learn something I did not know. The latter is not the case. Don't let the reader think the former. Don't use this acronym.

Accepted with thanks. We replaced 'LNAT with 'liquid-NAT mixture' throughout the manuscript as followed in Pitts et al., (2018).

Reference:

Pitts, M. C., Poole, L. R., & Gonzalez, R. (2018). Polar stratospheric cloud climatology based on CALIPSO spaceborne lidar measurements from 2006 to 2017. Atmospheric Chemistry and Physics, 18(15), 10881–10913. https://doi.org/10.5194/ACP-18-10881-2018

123 What usually occurs at ~-80°? In the example shown the intersection is at -83° or so.

Revised. Since, the current methodology to retrieve the PSC formation pathways doesn't restrict only to the intersection point of two CALIPSO scan track, hence the old "Sect 2.3 Retrieval of formation pathways" is removed and new methodology is given in Sect 3.3., L183 of page no. 6 to L240 of page no. 7 in the revised manuscript.

143 How are the vertical levels chosen and why only three? It seems there could be a number of vertical levels involved depending on the temperature structure.

In lower stratosphere, the air parcel mostly remains in same isentropic level for 'short duration' of period. Also, the vertical ascent/descent rate of air parcels is also too low such that within the period of 4 h (which is time interval between two CALIPSO observation at intersection points). Hence, it is less likely that the air parcel carrying the PSC of certain class would go from one isentropic level to another.

For example, if we observe air parcel carrying the 'ice PSC' at the altitude of 15 km (which corresponds to potential temperature of 375 K), it is highly likely that the air parcel was at the same altitude for the last 4 hr, given the slow ascent/descent rate. However, there may be a situation, the air parcel would travel slightly above or below the current level i.e., from 15 km in current example. Hence, instead of taking the altitude of 15 km alone, we chosen 1 level above and below as a conservative measure which is three consecutive vertical levels.

However, since we changed the methodology to track the individual air parcels using CLaMS trajectory module, we no longer considering either horizontal or vertical boundary.

144-145 Limiting the classification to only the most populated PSC type biases the results to only the dominant PSC kind. The different kinds of PSCs in any one air volume is not noise. It is not at all clear that this simplification provides any vital information about PSC formation pathways, rather it masks the reality.

Thanks for the comment. We acknowledge the issue of possible biases. Hence, in this revised manuscript, we estimated the backward trajectory using CLaMS trajectory module and filled the PSCs along the trajectory using coinciding CALIPSO observation. This way, we no longer do reclassification of PSC type.

According to Pitts et al. (2018) the CALIOPI data are averaged along track over 5, 15, 45, and possibly 135 km between 8.5 and 30 km to obtain a PSC classification. Here the authors downgrade these observations of 5 possible PSC classes (No Cloud, STS, NAT mixtures, enhanced NAT mixtures, ice) across an along track distance of 300 km, before and after the intersection point from the Nth scan to the Nth+2 scan, and at 250 m vertical resolution to just one PSC class. So roughly for each CALIOPI intersection point two measurements each containing at a minimum some 2000 possibilities (600/135 * (30-10)/0.25 * 5 = distance

intervals * altitude intervals * PSC classes) is reduced to two classifications. This generalization is way too simplistic.

We agree with the reviewer comment that the generalization is simplistic and may mask the reality as the 5 possible PSC classes is reduced the single most dominant PSC class. Hence, as discussed earlier, we modified the methodology such that, we no longer do the reclassification. Instead, we calculated the backward trajectories of each ice and liquid-NAT mixture and studied their complete evolution using temperature history, MLS HNO_3, H_2O and corresponding CLaMS model simulation. The detailed methodology is provided in Sect 3.3., L183 of page no. 6 to L240 of page no. 7 in the revised manuscript.

158-159. The intersection points occur over a range of latitudes < -80. State the range, not just that they are close to -80, which clearly from Fig. 1 they are not.

The latitude of the intersections point varies between -81° and -76°. However, the intersections points of the CALIPSO scan tracks are not considered anymore to study the PSC formation pathways. Instead, we use calculated backward trajectories of ice/liquid-NAT mixture PSC to understand their formation pathways.

162 It is clear how the horizontal boundary is selected, but not how the vertical interval is selected. It was ambiguous before and remains so.

Explained in the previous comment concerning the selection of vertical intervals.

163-164 This is speculation about NAT rocks without any basis. In fact there is information in the first scan masked by the requirement that the most populated category, in this case NC, is used to characterize all the scans.

Thank you for the comment. As discussed in response to comment #2, we no longer characterize the air parcels with most populated PSC class in the revised methodology. Through this, we avoid masking the less populated PSC with most populated PSC class.

165-166 This is way too simplistic. What are the temperatures in the first and second scans? How much did the air move in this period? Where did it come from? Were there already vestiges of PSCs in the first scan? Are the first two scans related to each other in any way? Did the air move from the first to the second, or from the second to the first? The authors could obtain all of this information which is germane to each specific measurement.

We have addressed this concern also in the modified methodology and analyses incorporated in the revised manuscript. We have now shown the complete picture of the PSC formation obtained through backward trajectories i.e. what is temperature before and during the observation of PSC, under which condition these PSCs are discussed in each cases (Case no. 1 to Case no. 7). In addition, further detailed study is carried out as described in methodology Sect 3.3.

166 … Similarly, all possible formation pathways of both ice and LNAT are retrieved during each successful intersection point… This has not been demonstrated or even discussed. Thus such a claim cannot be made.

Addressed with thanks. In the revised manuscript, we discuss in detail about the formation pathways of ice and liquid-NAT mixture and detailed methodology is given in Sect 3.3.

168-175 This is idle speculation and should all be eliminated. Anyone studying PSCs already knows that temperature and gaseous constituents are the most important items. That is what the introduction is for.

Complied with.

178-179 … as described in Sect. 2.3, we accounted for changes in these parameters when retrieving the PSC formation pathways … This is not true. Where were these accounted for? Temperature was for example never mentioned.

We apologize for the confusion caused here. In original manuscript, in Sect 2.3, at L172 to L174, we mentioned that considering the change in temperature is important to conclude possible PSC formation pathways. Those lines are, "Hence, to conclude which formation pathway is responsible for the specific PSC formation, it is essential to consider the corresponding change in temperature and gaseous species also, as described in the next section."

In the subsequent Sect 2.4 at L178 to L179, we written "The change in air temperature and gas-phase HNO_3 mixing ratio offer valuable insight into potential PSC formation pathways, as described in Sect. 2.3, we accounted for changes in these parameters when retrieving the PSC formation pathways (Nakajima et al., 2016).". The confusion could have been avoided if this sentence is separated in two to enhance clarity. So, the clear version is, "The change in air temperature and gas-phase HNO_3 mixing ratio offer valuable insight into potential PSC formation pathways, as described in Sect. 2.3. Hence, we accounted for changes in these parameters when retrieving the PSC formation pathways (Nakajima et al., 2016)."

However, both the Sect. 2.3 and 2.4 are removed now, as we changed the methodology to retrieve the PSC formation pathways. The updated methodology is given in Sect. 3.3.in page no. 6. In the updated methodology, we consider the temperature history of the air parcels such as ambient temperature, T_{ice}, and T_{NAT} to gain information about the formation pathways.

Reference:

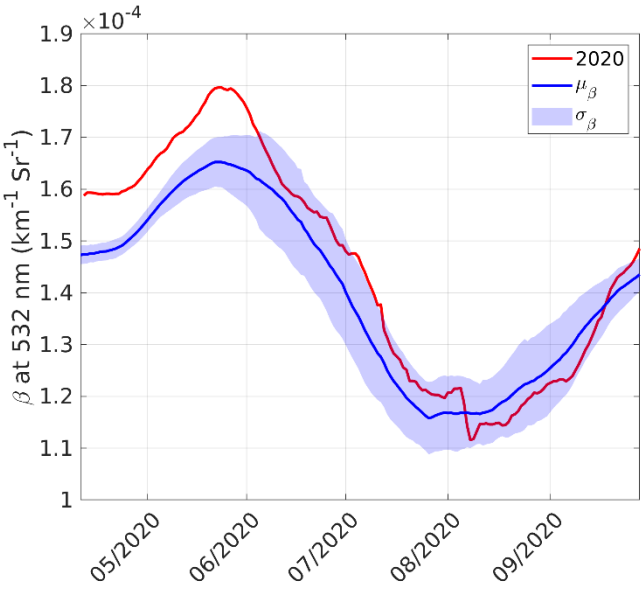
Nakajima, H., Wohltmann, I., Wegner, T., Takeda, M., Pitts, M. C., Poole, L. R., Lehmann, R., Santee, M. L., and Rex, M.: Polar stratospheric cloud evolution and chlorine activation measured by CALIPSO and MLS, and modeled by ATLAS, Atmos Chem Phys, 16, 3311–3325, https://doi.org/10.5194/ACP-16-3311-2016, 2016.

215-216 … Since April 2020, a negative anomaly of kext has been observed at the latitude ~-80°, which is attributed to the nucleation of PSC on these aerosols (Zhu et al., 2018)…. It is not clear on the figure that this is the case. In April 2020 the colors are yellow and white, which straddle zero. Is this what the authors

are pointing to? Also OMPS is struggling to reach -80 degrees in April, unlikely that the measurements extend beyond the middle of April. In any case if PSCs formed wouldn't this increase the extinction? Is it Zhu et al. who attributed the nucleation of PSCs on these aerosols or the authors here?

Please note that we have used the cloud filtered OMPS extinction coefficient for the current analysis, accounting only for aerosols. Hence, increase in PSC during April 2020 is not reflected in anomaly in k_{ext} from OMPS because they are filtered off i.e., some of the aerosols would have gone into the cloud and manifest as cloud and thus have been filtered off. For this reason, the decreased Δk_{ext} (during April 2020 at latitude < -80°) is attributed to reduced aerosol loading as these aerosols acted as nuclei for PSC formation and resulted in more PSC areal coverage. Similar argument is made by Zhu et al., (2018) who has first suggested that aerosols from Calbuco volcano eruption 2015 increased stratospheric sulfuric acid aerosol abundance, and possibly led to more PSC formation. We findings are corroborates the results by Zhu et al., (2018).

In addition, as the OMPS is passive satellite, it does not provide data at high-latitude during winter period. To address this, we used CALIPSO total attenuated backscatter (sum of parallel and perpendicular backscatter) to understand the magnitude of impact of bushfire aerosol during PSC formation period i.e., May to September 2020 and shown the result in Fig. 6 in this revised manuscript and also shown below.



The above plot shows the anomaly in CALIPSO observed total attenuated backscatter (β) at 532 nm corresponding to grids classified as 'No Cloud (NC)' at the temperature above T_{NAT}. Here, 'σ_β' (blue shading region) represents the standard deviation with respect to the background mean 'μ_β' (solid blue line) estimated for the period 2009–2019. The solid red line corresponds to the 2020 daily mean. The x-ticks mark the middle of each month.

To plot the above figure, we chose the total attenuated backscatter corresponding to CALIPSO for grids classified as 'No Cloud (NC)' only if their temperature is above the $T_{NAT,}$ as it removes contribution from sub-visible PSC (Lambert et al., 2012) and gives clear signal about the stratospheric aerosol. During May to mid-June 2020, the total attenuated backscatter (varies between 1.6×10^{-4} and 1.8×10^{-4} (km^{-1} Sr^{-1}) is higher by more than one standard

deviation with respective to the background mean and after mid-June, the total attenuated backscatter of 2020 became comparable to background mean. This significant increase in total attenuated backscatter during May–June 2020 and corresponding decrease of the same after that suggests the involvement of at bushfire aerosols in PSC formation process. In the revised manuscript, this plot and corresponding discussion is given at L464 to L 476 of page no. 17.

216-217 … The kext increased again at high latitudes in October and November 2020 which is due to the re-release of the captured aerosols by the PSC, … This is pure speculation and makes no sense. If PSCs evaporate the particles get smaller and extinction decreases.

Thank you for the comment. We agree with the reviewer that as the PSC evaporate the particle get smaller and extinction decreases. Sametime, they would now add to the cloud-filtered OMPS aerosol extinction, leading to an increase in k_{ext} corresponds to the stratospheric aerosol.

253-255 The water vapor decrease doesn't really begin until late winter and then extends through spring to summer long after PSCs are a factor. The change in HNO3 is more indicative of being impacted by PSCs, but how is the 2020 winter different than others in this regard, since HNO3 is always observed to begin decreasing about this time at these altitudes? Linking this observation to the presence of brush fire smoke is too simplistic and is not verified by these observations.

We would like to clarify that through Fig. 5 in old manuscript (which is Fig. 3 in revised manuscript), we are discussing the anomaly in HNO_3 and H_2O, but not the actual observed mixing ratios of these gases. In addition, during 2020, both HNO_3, and H_2O also decreased at the beginning of the winter as it usually happens (plot not shown in manuscript). However, unlike H_2O, mean HNO_3 is increased by 1.5 ppb on compared the background period during early 2020 (Fig. 3 (a) in revised plot). This is due to the increased surface area provided by the bushfire aerosols which led to enhanced N_2O_5 hydrolysis process, releasing more HNO_3. The evidence of production of HNO_3 due to enhanced N_2O_5 hydrolysis process is show in Fig. 4 and 5 in the revised manuscript. But all these excess produced HNO_3 depleted by June 2020, suggesting the condensation of this gas into PSC, and finally increased the PSC areal coverage (shown in Fig. 7 in revised manuscript). This makes this 2020 winter different from previous years.

The observed strong negative anomaly in HNO_3, and H_2O during later-winter to spring 2020 is attributed to the prolonged polar vortex during 2020, and not relative to the PSC formations.

Fig. 6 and discussion. What are the latitude/longitude bounds for the data shown? Why were these particular altitudes chosen? Were others looked at and these deemed to be representative or?

We have now added the bounds in the revised manuscript. The latitude bounds are from -60° to -90° for all longitudes. We have included the latitude range in the figure caption (L421to L 425, page no. 15). The updated figure caption reads as below.

"*Figure 4: Tracer-trace correlation between ACE-FTS (a) HNO_3 and HF at the altitude of 25 km, and (b) H_2O vs HF at the altitude of 17 km corresponds to latitude range from -60° to -90°. The blue circles correspond to the*

period March of 2009–2019, the red diamonds to the period March 2020, and the solid black line is a regression line. Here, 'N' is the number of data points used for regression analysis for both subplots."

The altitude of 25 km is chosen for HNO_3, because ΔHNO_3 peaked around this altitude during March 2020 (Fig. 3 (a) in revised manuscript). Similarly, ΔH_2O peaked at the altitude of 17 km for the same period (Fig. 3 (b) in revised manuscript).

298 Fig. 7a) shows OMPS extinctions, not n2o5.

Sorry, and thank you for pointing out. We changed the panel number from (a) to (c) which shows N2O5 now at L437 in page no. 16.

Fig. 7 What time period is represented by the blue lines and shading? What does the shading indicate?

The blue line represents background mean estimated using the period 2009-2019 and blue shading corresponds to the one standard deviation with respect to the background mean. We have included these in the caption of Fig. 5 in revised manuscript. The revised figure caption is

"*Figure 5: OMPS obtained (a) k_{ext} at 745 nm, and ACE-FTS obtained (b) HNO_3, (c) N_2O_5, and (d) H_2O mixing ratio at the altitude 25 km averaged between the latitude band -60° to -90°. Here, 'σ' represents the standard deviation with respect to the background mean 'μ' estimated for the period 2009–2019. The x-ticks mark the middle of each month"*

317 … The near-simultaneous decrease in aerosol loading (as discussed in Sect. 3.2), … Where is this shown? It is not substantiated by Figs 3 or 4. In fact OMPS can provide little aerosol data at PSC relevant latitudes in austral winter.

Thank you for the comment. Since OMPS does not provide much data over high latitude region where PSC forms during Austral winter, we have used the CALIPSO total attenuated backscatter corresponding to NC grids whose temperature lies above T_{NAT} as discussed in the reply to earlier comment (please see response to comment #14) Furthermore, detailed discussion is included in page no. 17 from L464 to L476.

333-335 These statement seem obvious. Any particle surface area promotes the chlorine activation reaction.

Thank you. We moved these lines from here to Sect. 2 where brief literature review about PSC is given (in L91 to L93 in page no. 3). The lines are quoted below.

"Among the different types of PSCs, liquid forms like STS, as well as other liquid stratospheric aerosols provide a surface for chlorine activating heterogeneous chemical reactions and play an important role in ozone destruction (Molina and Rowland, 1974; Molina et al., 1993; Ravishankara and Hanson, 1996; Ansmann et al., 2022; Wang et al., 2023)."

335-336 Wasn't enhanced ozone loss observed in 2020? Why not reference that paper? The references chosen are really just background information on STS, not so applicable here and should have already been covered in the introduction.

Complied with.

337-339 Here ENAT has a very small anomaly in July and August between 0 and 1 (x1e6 km2) yet the standardized anomaly exceeds three standard deviations, which calls into question the usefulness of the standardized anomaly. Note that it matches or exceeds SA of STS which has a much higher anomaly.

The standardized anomaly for each PSC type suggests how significant/important that the observed anomaly in PSC areal coverage. The high (low) standardized anomaly suggests that the observed anomaly is significant (insignificant). During July and August 2020, the enhanced NAT mixture anomaly is varied between 0 and 1 ($\times 1E^6$ km^2). We agree with reviewer's review that this magnitude of anomaly is low when compared to other PSCs such as STS, ice, and liquid-NAT mixture. But the standardized anomaly of enhanced NAT mixture says, it is significant because the areal coverage of the PSC significantly exceeded the background variability.

338-339 …It is evident from Fig. 8 that the positive anomalies in the areal coverage of PSCs like ice, STS, and ENAT exceeded three standard deviations with respect to the background mean… Correct, and yet some of these differences are important and others are not. It is difficult to know how to interpret the standardized anomaly. If the standard deviation is small the standardized anomaly will be large.

Yes. Since the standardized anomaly is ratio between the anomaly and one standard deviation, large standardized anomaly implies relatively larger anomaly is observed with respect to standard deviation (i.e. year to year variability).

It is true that anomaly in enhanced NAT mixture areal coverage also exceeded three standard deviations (as shown in Fig. 7 in page no. 18 in revised manuscript. Yet we consider it is not important for the present study. Hence, we did not concentrate on it for the following two reasons:

1. The enhanced NAT mixture contributes just 5.8% to the total PSC areal coverage as shown in Pitts et al., (2018).
2. Denitrification is not primarily driven by enhanced NAT mixture owing to their high number density and small size. Furthermore, chlorine activating heterogeneous reaction predominantly occurs on stratospheric aerosols and on liquid PSC. Hence, it does not play important role in ozone depletion process.

343 Again there is no such thing as a liquid nitric acid trihydrate. It is an oxymoron. Hydrate implies a solid particle. Weren't all these acronyms already defined anyway?

Thank you for the comment. As mentioned in response to comment #1, we replaced 'LNAT' with 'liquid-NAT mixture' throughout the manuscript now.

375-385 There are numerous problems with this discussion. First there is no nucleation barrier for STS it is a liquid solution droplet of water, hno3 and h2so4. Second all of these explanation have either already been repeated or should have appeared in the introduction and background on PSCs. We agree to the view with thanks. We have removed these from the discussion. As mentioned in the beginning of these responses, we have included a new section "2" on the literature review about the PSCs formations which are between L71 of page no. 3 and L132 of page no. 4.

Third the authors here use a very simplistic approach of attributing all of a particular CALIOPI observation to the most dominant particle in the observation. Thus NC may well contain PSC particles, they just don't happen to be the dominant ones.

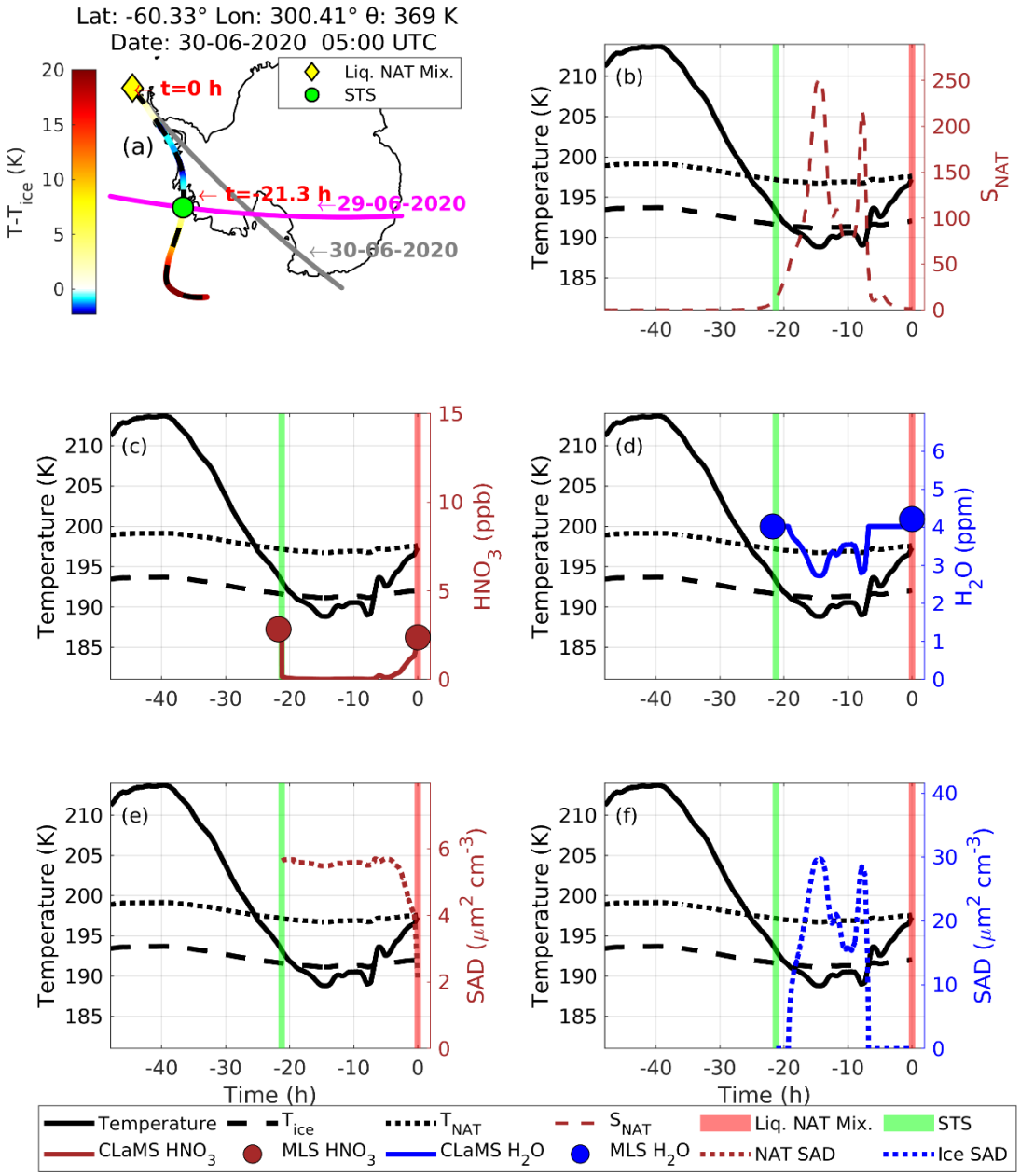
To address this issue, we changed from the earlier simplistic approach of retrieving PSC formation pathway at the intersection points of CALIPSO scan track to Lagrangian backward trajectory analysis combined with CLaMS microphysical box model simulation. Since, we track the individual air parcel leading to formation of ice/liquid-NAT mixture, we no longer do the reclassification as did in original manuscript.

Fourth do the changes in temperature make sense to convert NC into a liquid NAT mixture based on the HNO3 and H20 available? This can be calculated.

As suggested by the reviewer, we checked whether the observed change in temperature during the formation of PSC (for both ice and liquid-NAT mixture) based on the HNO_3, and H_2O availability. For this, we taken the temperature belongs to the backward trajectories of liquid-NAT mixture, and ice PSC and fed into the CLaMS box model. The CLaMS modelled uptake in HNO3, and H2O are compared with MLS observed uptakes of these gases during the formation of both ice and liquid-NAT mixture PSCs. The result shows that there is good agreement between the MLS observed and CLaMS modelled uptakes. The scatter plot comparing the modelled and observed uptakes along with linear regression analysis are shown in Fig. 12 (for liquid-NAT mixture formation) in page no. 28 and Fig. 18 (for ice formation) in page no. 38 in revised manuscript.

Fifth the spread in the temperature data to convert from NC-LNAT is from -1 to 0.8 K for the interquartile range. So LNAT forms even though the temperature increases from a NC situation? This alone should give the authors pause.

We understand the question regarding observed increase in temperature during 'NC to liquid-NAT mixture' transition. In our new analysis, we found that there are instances where NC/STS preceded the liquid-NAT mixture along the backward trajectories. During these cases, the ambient temperature during at the time of observation of liquid-NAT mixture is found to be relatively higher than at the time of observation of NC/STS. This is because, temperature history of the air parcels (i.e., how long the temperature of the air parcel remains below T_{NAT} and whether it decreased below Tice or not) play as a crucial factor during PSC formation rather than the difference between the temperature during two observations. We would like to demonstrate this using a case where during the formation of liquid-NAT mixture from STS. On 30-06-2020, at 18:00 UTC, CALIPSO detected a liquid-NAT mixture at a latitude of -60.3° and longitude of 300.41°, with a potential temperature of 369 K. This observation is marked by a yellow diamond in panel (a) of plot shown below and corresponding CALIPSO scan track is shown as a solid grey line. The dashed black line in panel (a) represents the calculated 48 h backward trajectory of this PSC, with the color indicating the temperature history of the air parcel in ice coordinates. The temperature 'T' is obtained from ERA5 operational analysis, and T_{ice} is estimated using the ERA5 pressure, and mean MLS H_2O mixing ratio found along the trajectory following Marti and Mauersberger, (1993).



In above plot, panel (a) shows the Lagrangian backward trajectory for a 48 h period starting at time, t = 0 h (corresponding to 05:00 UTC 30-06-2020) is shown. Here, the dashed black line is the backward trajectory and the color along this trajectory is the temperature at the T-T_{ice} coordinate. The yellow diamond represents the observed liquid-NAT mixture from the CALIPSO scan track (solid grey line) corresponding to 30-06-2020. The complete coordinate of this liquid-NAT mixture is given in the title. The green circle represents the observed 'STS' at the time, t = -21.3 h from the CALIPSO scan track (solid magenta line) corresponding to 29-06-2020. (b) shows the saturation ratio over NAT (S_{NAT}) (dashed brown line) and vertical bars mark the liquid-NAT mixture (red) and STS (green). (c) The brown circle marks the MLS HNO_3, and the solid brown line represents the CLaMS HNO_3. (d) The blue circle marks the MLS H_2O, and the solid blue line represents the CLaMS H_2O. (e) shows the NAT surface area density (SAD) (dotted brown line). Panel (f) shows the ice surface area density (SAD) (dotted blue line).

The backward trajectory revealed that CALIPSO observed STS along this trajectory 21.3 hours earlier (at the time, t = -21.3 h), on 30-06-2020, marked by a green circle in panel (a). The temperature history shows that between these two observations, the temperature decreased below the T_{ice}, indicating that the condition is conducive for ice formation. At the time of the STS observation, the temperature is ~193 K which is below the NAT temperature (T_{NAT}). During this time, MLS observed gas-phase HNO_3 and H_2O mixing ratios are 2.7 ppb and 4 ppm, respectively (panel (c) and (d)). Using these as initial conditions, a CLaMS box model run was performed from t = -21.3 h to 0 h, simulating the evolution from the STS to the liquid-NAT mixture. After 21.3 h, the MLS HNO_3 decreased from 2.7 to 2.4 ppb, with no significant change in MLS H_2O. The CLaMS modeled uptake of HNO_3, and H_2O agreed well with the MLS observations (panel (c) and (d)). Furthermore, the CLaMS box model run indicates that the NAT surface area density (SAD) increased to nearly 6 $\mu m^2\ cm^{-3}$ (panel (e)), while the ice SAD increased up to 30 $\mu m^2\ cm^{-3}$ when temperature remained below T_{ice}, suggesting the ice formation occurred before the observation of the liquid-NAT mixture and these NAT could have formed via ice-assisted formation pathway.

This case reveals two things:

1. Firstly, the temperature at the time of observation of STS is 193 K, but at the time of observation of liquid-NAT mixture is 197.5 K which is almost 4.5 K higher than the temperature observed during STS detection. Even though, the net temperature increased, as it remained below T_{NAT} for ~20 hr and even decreased below T_{ice}, the condition favoured the formation of liquid-NAT mixture.
2. Secondly, even though the STS is observed to precede the liquid-NAT mixture observation along the trajectory, this case belongs to ice-assisted NAT nucleation. This is because, between the CALIPSO observation of STS and liquid-NAT mixture, the temperature of the air parcel decreased below T_{ice}, forming ice. After that, when temperature increased above Tice, NAT particles possibly nucleated on the ice particles. Hence, it is crucial to consider temperature history to conclude the formation pathway of PSC.

More cases like these are discussed in the revised manuscript. Liquid-NAT mixture formation pathway cases are discussed from page no. 19 to 27 (through Case no. 1 to 4), and ice formation pathway cases are discussed from page no. 31 to 35 (through Case no. 5 to 7). We hope this shall strengthen the discussion section.

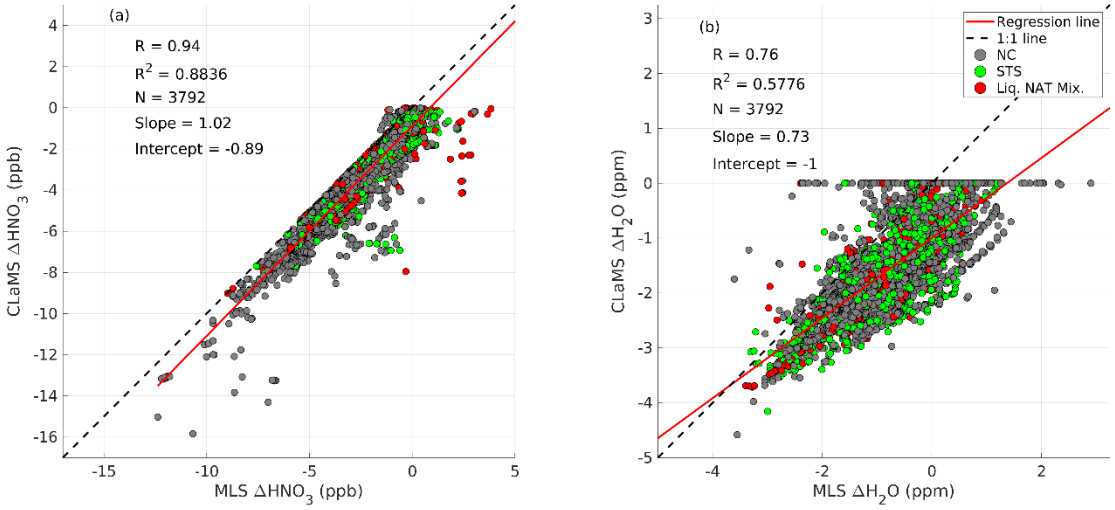
References:

Marti, J., & Mauersberger, K. (1993). A survey and new measurements of ice vapor pressure at temperatures between 170 and 250K. Geophysical Research Letters, 20(5), 363–366. https://doi.org/10.1029/93GL00105

390-480 Here the authors carry on with their discussion of the different PSC formation pathways, but without providing anything more than statistical broad brushes and without any quantification checks. For example, are the temperature changes consistent with the changes in hno3 concentrations for various transitions. The final conclusion seems to be.

Thank you for the comment. Based on the suggestion of the reviewer, we have validated the observed change in HNO_3 and H_2O mixing ratio against the CLaMS modelled uptake and results are discussed in Sect. 4.5.3 (for liquid-NAT mixture) and Sect. 4.5.9 (for ice) in detail. Here we show a key plot for ice (the details discussion of the same plot is given in revised manuscript, Sect 4.5.9 in page no. 38).

A strong correlation is found between the MLS observed change in HNO_3 (ΔHNO_3) and the CLaMS modeled change in HNO_3, with a correlation coefficient (R) of 0.94 and a coefficient of determination (R^2) of 0.8836 (panel (a)). A significant HNO_3 uptake of up to 12 ppb, as observed by MLS, occurs when NC preceded the observation of the ice along the trajectory (indicated by the grey circle in panel (a)). In contrast, a relatively low HNO_3 uptake is noted when STS (liquid-NAT mixture) preceded the ice formation which is marked with the green circle (red circle) in panel (a). In the case of H_2O uptake, a good correlation is found between MLS ΔH_2O and CLaMS ΔH_2O, with a correlation coefficient (R) of 0.76 and a coefficient of determination (R^2) of 0.5776 (panel (b)).



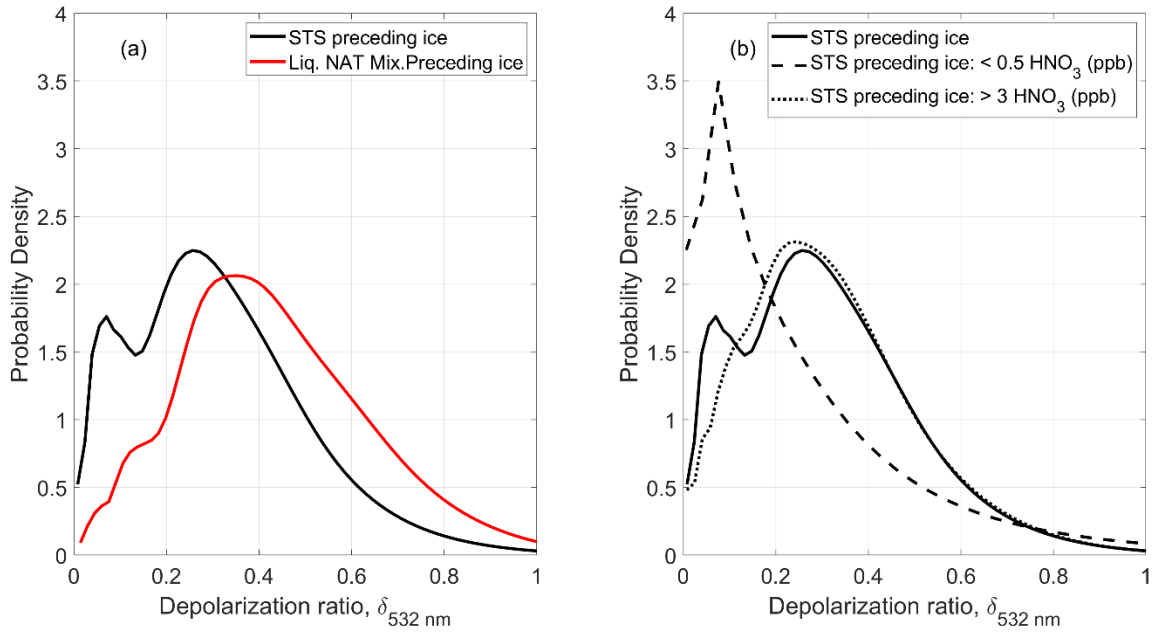
In above plot, panel (a) shows a scatter plot of MLS observed change (Δ) in HNO_3 (ppb) against the CLaMS modeled change in HNO_3 (ppb) during the ice formation. Panel (b) shows a scatter plot of MLS observed change (Δ) in H_2O (ppm) against the CLaMS modeled change in H_2O (ppm). The dashed line represents a 1:1 fit, and the solid red line represents the linear regression line. Here, 'R' is the correlation coefficient, 'R^2' is the correlation of determination, and N is the total number of data points used. The color of the circles corresponds to each PSC type preceding to ice along the backward trajectory. Grey for NC, green for STS, and red for liquid-NAT mixture.

…From the above discussions, it is clear that the majority of the LNAT (82 %) and ice (77 %) are formed through 'NC-to-LNAT' and 'LNAT-to-Ice' pathways respectively. It indicates that LNAT nucleated on the stratospheric aerosols, which subsequently acted as nuclei for ice formation. Moreover, the 'LNAT-to-Ice' conversion should have occurred rapidly to explain the high anomalous ice areal coverage. In fact, both 'NC-to-LNAT' and 'LNAT-to-Ice' pathways are parts of the three-stage PSC formation model (Peter, 1997). …

So what is new here? If we get past the LNAT acronym to remember what Pitts et al.'s classification is, we find it is a liquid-NAT mixture. The only liquid PSC is also known as STS so it is an STS-NAT or a sulfuric acid water and NAT mixture with a depolarization ratio too high to be STS alone. So as the air cools some NAT forms and at about 3K below Tnat STS forms giving us this mixture. Then if temperature continues to cool to about 6 K below Tnat some ice may form. The extent to which NAT and ice form is dependent on the availability of NAT and ice nuclei. These can be as the authors point out meteoric dust, sulfuric acid and water with unusual inclusions, or possibly hydrates of sulfuric acid, although these have never been observed in the atmosphere, or some unknown particle type. But all this follows the three stage PSC formation model as has been documented in the literature over many observational, laboratorial, and theoretical papers. What is new here? If PSCs form in any air mass they will be some combination of NAT and STS, e.g. LNAT in this paper's acronym, and if it cools further ice is likely to form. How has this analysis shed new light on these processes? In fact the generalizations are so broad in the initial classification scheme that these statistical analyses of the temperatures and hno3 concentrations can hardly lead to any useful new information.

We thank the reviewer for the detailed comment. We would like to highlight the key findings from revised methodology related to the formation pathways of PSCs below.

1. We report 79 % of liquid-NAT mixtures formed through ice-free nucleation with high confidence, as no ice PSCs observed along the backward trajectories and temperature remained above the ice formation threshold (T_{ice}-1.5K). Whereas 12 % of liquid-NAT mixtures formed via ice-assisted nucleation with high confidence, as CALIPSO observations of ice PSCs before liquid-NAT formation and 9% with low confidence, as the temperature dropped below the ice formation threshold but no direct ice PSC observation.



In the above plot, panel (a) shows the probability density of the depolarization ratio of ice preceded by STS (solid black line) and liquid-NAT mixture (solid red line) are shown. Panel (b) shows decomposition of ice preceded by STS cases based on MLS HNO_3 mixing ratios: < 0.5 ppb (dashed line) and > 3 ppb (dotted line).

2. We observed that depolarization ratio of ice PSC to exhibit bimodal distribution for the cases where ice is preceded by STS along the backward trajectories. Further analysis on this revealed that, the low depolarization ratio mode (peaked at ~0.07) corresponds to ice nucleation on STS under denitrified conditions (HNO_3 < 0.5 ppb). High depolarization ratio (peaked ~0.26) corresponds ice nucleation on NAT under normal conditions (HNO_3 > 3 ppb). A similar bimodal distribution in depolarization ratio of ice PSC is observed by Voigt et al., (2018) during the HALO campaign over Arctic region and the author suggested that ice with low depolarization ratio could have formed by nucleating on STS, and high depolarization ratio via nucleating on NAT. It shows that our results are aligned with previous field observation. (Please kindly see Sect. 4.5.8 for more discussion on bimodal distribution of depolarization ratio)

3. We report 13.86 % of ice PSCs formed via NAT-assisted nucleation with high confidence, as presence of liquid-NAT mixtures are observed through CALIPSO along the backward trajectory of these ice PSCs. Almost 38.02 % with medium confidence, as there is no direct CALIPSO observation of present of liquid-NAT mixture but significant HNO_3 availability > 3 ppb, hence high likelihood of NAT formation, and 43.42 % with low confidence, as HNO_3 varies between 0.5 and 3 ppb). Thus, NAT-assisted ice formation pathway accounts for ~95.31 % of ice PSC. And just 4.69% of ice PSCs formed via NAT-free nucleation under extremely denitrified conditions (HNO3 < 0.5 ppb), as not enough HNO_3 availability for NAT formation and thus these ice PSCs should have nucleated on STS with possible inclusion of foreign nuclei.

References:

Voigt, C., Dörnbrack, A., Wirth, M., Groß, S. M., Pitts, M. C., Poole, L. R., Baumann, R., Ehard, B., Sinnhuber, B. M., Woiwode, W., and Oelhaf, H.: Widespread polar stratospheric ice clouds in the 2015-2016 Arctic winter - Implications for ice nucleation, Atmos Chem Phys, 18, 15623–15641, https://doi.org/10.5194/ACP-18-15623-2018, 2018.