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:

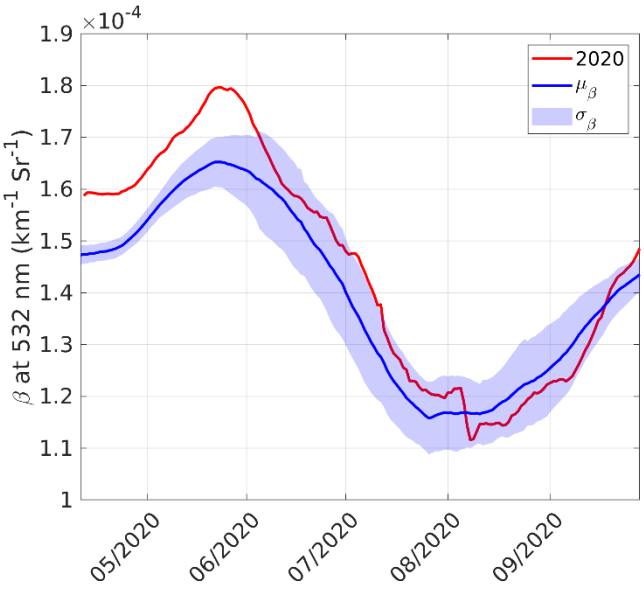
Nakajima, H., Wohltmann, I., Wegner, T., Takeda, M., Pitts, M. C., Poole, L. R., Lehmann, R., Santee, M. L., and Rex, M.: Polar stratospheric cloud evolution and chlorine activation measured by CALIPSO and MLS, and modeled by ATLAS, Atmos Chem Phys, 16, 3311–3325, https://doi.org/10.5194/ACP-16-3311-2016,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

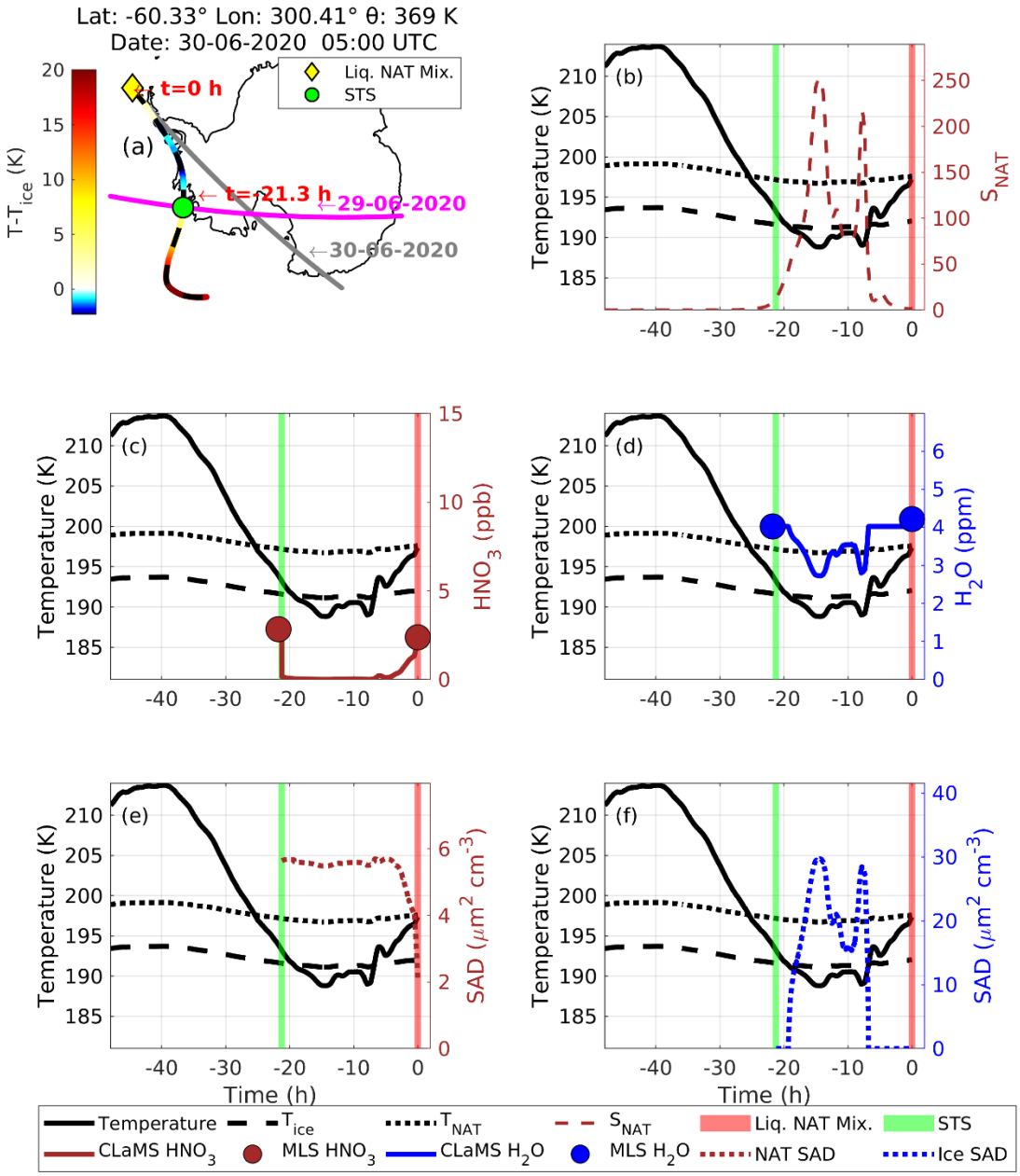
To address this issue, we changed from the earlier simplistic approach of retrieving PSC formation pathway at the intersection points of CALIPSO scan track to Lagrangian backward trajectory analysis combined with CLaMS microphysical box model simulation. Since, we track the individual air parcel leading 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.

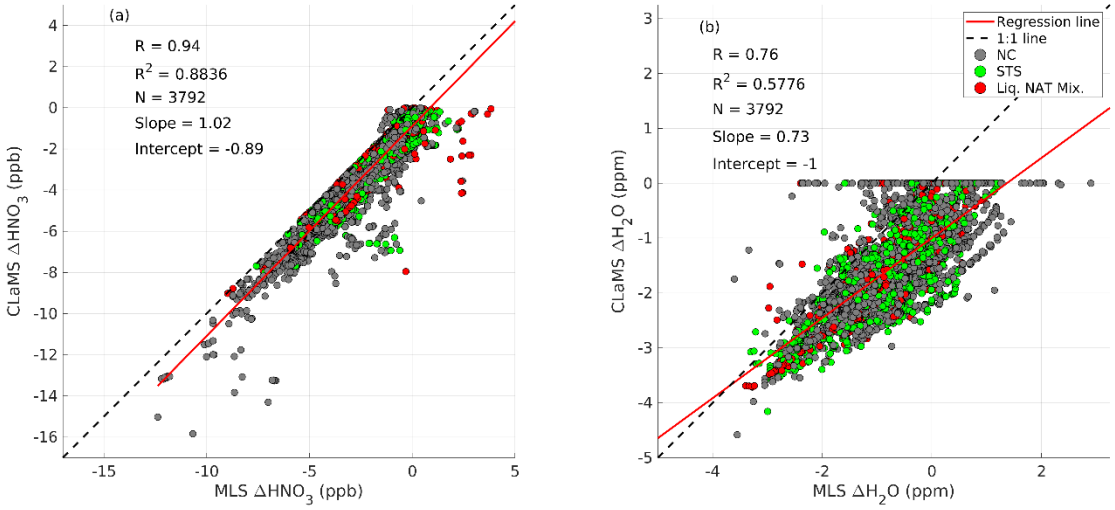
References:

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)).



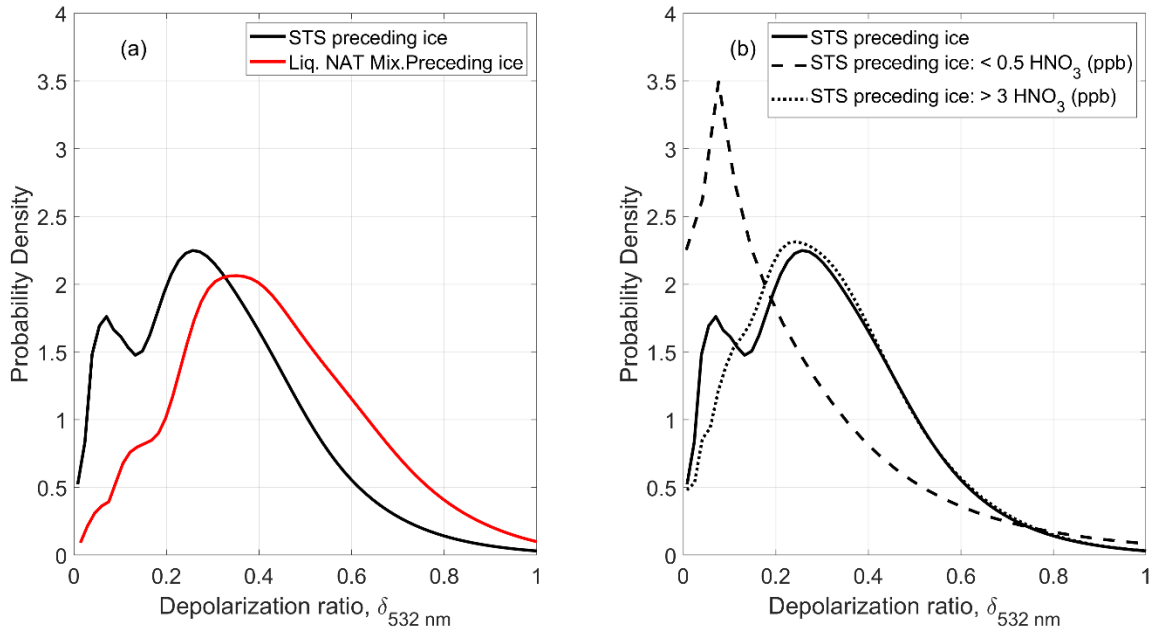
In above plot, panel (a) shows a scatter plot of MLS observed change (Δ) in HNO_3 (ppb) against the CLaMS modeled change in HNO_3 (ppb) during the ice formation. Panel (b) shows a scatter plot of MLS observed change (Δ) in H_2O (ppm) against the CLaMS modeled change in H_2O (ppm). The dashed line represents 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.

Author response to Reviewer #2 comments

We sincerely thank the reviewer for the comments. Based on the comments we have carefully revised 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 #2

This paper describes the impact of Australian extreme bushfire event during 2019/2020 on Antarctic PSC occurrence and subsequent ozone hole in 2020. It is a new idea to investigate the influence of extreme bushfire on Antarctic PSC formation. However, since the author discuss only one winter (2020), the discussion and conclusions that the authors mentioned in the paper is not very convincing. At least, the authors should analyze another year when the Antarctic ozone depletion is about the same magnitude as 2020 (for example, 2021 or 2022), and compare the results with those in 2020.

We thank the reviewer for the valuable comments and appreciation as well as the suggestion to extend the work to another year. But unfortunately, the CALIPSO PSC V2 product, which is used in the present work is available only till March 2021, and not beyond. As such, we could not carry out this study for 2021/ 2022.

However, now we have strengthened the discussion and conclusion section by performing the Lagrangian backward trajectory analysis to study the PSC formation pathways and also simulated the PSC formation using CLaMS microphysical box model (complying with the comments of reviewer #1) to validate the Microwave Limb Sounder (MLS) observed uptakes of HNO_3, and H_2O against the modelled uptake during formation of ice and liquid-NAT mixture PSC and included in the revised manuscript (also please see the responses to reviewer #1 in this regard). The details are as below:

First, we calculated the 48 h backward trajectories of ice and liquid-NAT mixture PSCs using CLaMS trajectory module with hourly ERA5 operational analysis meteorological data. Using the trajectories, we identified which type of PSC preceded the initial PSC (ice/liquid-NAT mixture) for which backward trajectory is estimated. The temperature history, uptakes of MLS HNO_3, H_2O mixing ratio during the formation of the ice/liquid–NAT mixture PSCs are studied. 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.

< Specific Comments >

1) P.3, L.72: MLS is a 5-band microwave radiometer, not a Fourier-Transform Spectrometer (FTS).

Thank you for pointing out this. We have made the necessary correction in the revised manuscript.

2) P.3, L.83: The authors used the terminology "Liquid Nitric Acid Trihydrate (LNAT)" throughout the paper. However, Nitric Acid Trihydrate is a solid PSC, not liquid at all. I assume that the authors are referring "Mix 1" or "Mix 2" PSCs in Pitts et al. (2009), which are the mixture of STS and NAT PSCs. The authors should not use the term "LNAT", but better use the term "Mix PSCs".

Thanks for pointing this out. We are sorry at using a confusing terminology (as also has been pointed out by the other reviewers) and have corrected it in throughout the revised manuscript. Now, instead of 'LNAT, we used 'liquid-NAT mixtures throughout the manuscript

3) P.7, L.204, Figure 3 caption: What is the definition of "standardized anomaly (Z)"? Please define Z by a equation.

The standardized anomaly (Z) is estimated as ratio between the anomaly (2020 – Background mean) and standard deviation estimated using background period. In the manuscript, it is given in equation no. 2 at line number 181.

4) P.8, L.214: What is the meaning of "additional"? In addition to what? Please explain.

Antarctic ozone depletion occurs during spring of every year and is attributed to the active halogens in lower stratosphere. Usually, the magnitude of ozone depletion (i.e. ozone loss) for a given year is estimated by subtracting ozone amount of September/October (i.e. spring period) from June of the same year. In addition to this usual normal ozone loss, additionally more ozone is lost during the year 2020 (Ansmann et al., 2022) and hence it is called as 'Additional ozone loss.'

Ansmann, A., Ohneiser, K., Chudnovsky, A., Knopf, D. A., Eloranta, E. W., Villanueva, D., Seifert, P., Radenz, M., Barja, B., Zamorano, F., Jimenez, C., Engelmann, R., Baars, H., Griesche, H., Hofer, J., Althausen, D., & Wandinger, U. (2022). Ozone depletion in the Arctic and Antarctic stratosphere induced by wildfire smoke. *Atmospheric Chemistry and Physics*, *22*(17), 11701–11726. https://doi.org/10.5194/ACP-22-11701-2022

5) P.8, L.222: What is the meaning of "additional"? In addition to what? Please explain.

Explained. Please see the response to comment #4

6) P.8, L.222; Fig S1: The year 2019 was a exceptional year when the Antarctic ozone loss was minimum (like the year 2002), due to the dynamical effect (split of polar vortex in early spring). The authors should not compare the year 2020 with 2019, but had better compare with another normal year (like 2021 or 2022). One suggestion is to show time-series plots not for 2019-2020, but show like 2020-2021.

Thank you for the comment. In Fig. S1, we are showing the anomaly in Antarctic ozone from September 2019 to December 2020. This period is chosen to show the sudden increase in lower stratospheric aerosol and subsequent change in temperature followed by the black summer event which occurred at end of December 2019 through Fig. 1 and Fig. 2. Here, we are not comparing the year 2020 with 2019 but intended to show the sudden changes. To

maintain consistency in chosen time period, we made the plot Fig S1 as well to start from September 2019 and end at December 2020.

7) P.11, L. 292: The authors claim that "increased H_2O is transport-related as the data are close to the linear fit". However, I felt that the 2020 H_2O data are also deviated upward from the linear fit.

Thank you for the comment. In case of HNO_3, the 2020 HNO_3 are extremely deviated from linear fit i.e., if we make another linear fit for 2020, it would be at least 40° with the linear fit line corresponding to background data. However, in case of H_2O, if we make another linear for 2020, this linear fit line would be less than 10° or less with the linear fit line corresponding to background data i.e., the deviation is not much stronger to conclude that H2O is chemically produced during 2020.

8) P.13, L. 331: The authors claim that "Followed by ice, the Supercooled Ternary Solution (STS) exhibited a high positive anomaly". However the presence altitudes of ice and STS are different (ice: 15-20 km, STS: below 15 km). STS are not "followed" by ice.

Thank you for the comment. By "Followed by ice", we tried to convey that ice PSC areal coverage increased to significantly with peak positive anomaly of 4×10^6 km^2. The magnitude of positive anomaly is higher than anomaly by other PSC. After that, STS PSC high positive anomaly of 3.5×10^6 km^2 as discussed in manuscript, L486 to L488, page no. 18.

9) P.13, L.334: The authors claim that "the STS areal coverage can … lead to additional ozone loss." However, since the appearance altitude of STS are mostly below 15 km, the additional ozone loss cannot be expected in such low altitudes.

It is true that most of the STS forms below 15 km altitude. But the STS PSC is also present at altitude of 16 to 25 km during early June 2020 (Fig. 7 (j–l)) which could provide surface for chlorine activation reaction leading to additional ozone loss. This is supported by results from Ansmann et al., (2022) who shown that around PSC height range of 14–24 km, additional ozone loss is observed in September–October 2020.

Ansmann, A., Ohneiser, K., Chudnovsky, A., Knopf, D. A., Eloranta, E. W., Villanueva, D., Seifert, P., Radenz, M., Barja, B., Zamorano, F., Jimenez, C., Engelmann, R., Baars, H., Griesche, H., Hofer, J., Althausen, D., & Wandinger, U. (2022). Ozone depletion in the Arctic and Antarctic stratosphere induced by wildfire smoke. *Atmospheric Chemistry and Physics*, *22*(17), 11701–11726. https://doi.org/10.5194/ACP-22-11701-2022

10) P.14, Figure 9: I am curious if the authors also show the similar plot to indicate the formation pathways of STS from other types of PSCs.

We appreciate the comment. In the lower stratosphere, it is the STS PSC which always forms first i.e., well before formation of ice/liquid-NAT mixture. Hence, in terms of STS formation pathways, it essentially does not require NAT/ice to act as nuclei for formation. But, it can form either homogenously or heterogeneously. For this reason, the formation pathways of STS are not discussed in the present study.

11) P.17, L.422: In the course of the formation of ice PSC, why uptake of HNO_3 occurs? Where the decreased HNO_3 goes to? Please explain.

It is explained as follows. Most of the ice PSCs form by nucleating on NAT particles as our study reveals. When temperature of the air parcel decreases, HNO_3 condenses forming STS first, followed by liquid-NAT mixture. This process leads to depletion of gas-phase HNO_3. Following the formation of the liquid-NAT mixture, if the temperature remains below T_{NAT} (the NAT existence temperature) or decreases further, the NAT particles continue to grow, leading to further depletion of gas-phase HNO_3. As temperatures decrease even further reaching below T_{ice}, these NAT particles act as nuclei for ice formation. Hence, even in the course of ice formation, depletion in HNO_3 is observed.

We discussed this in detail through a case study (Case no. 4; Page no. 26; Fig. 11). In this case, we show that, initially temperature of the air parcel is above T_{NAT} and no PSC is formed by this time as confirmed by CALIPSO observation. When temperature decreased well below T_{NAT}, NAT particles appeared first as revealed by CLaMS box model run (Fig. 11 (e)). As the temperature decreased below T_{ice}, ice PSC formed (Fig. 11 (f)). During this ice formation process, ~5 ppb of HNO_3 is depleted.

12) P.18, L.457: The authors claim that "explain the high anomalous ice areal coverage." However, not reference nor supporting material/figure are shown to support the "high anomalous ice areal coverage" in 2020. Please show anything to explain that ice areal coverage in 2020 was anomalously high compare with other years.

Thank you for the comment. In the manuscript, at page no. 18 Fig. 7 shows the CALIPSO observed PSC areal coverage (first column), corresponding anomaly with respect to background period (second column), and standardized anomaly (third column). In this figure, ice PSC areal coverage (Panel a), anomaly (Panel b), and standardized anomaly (Panel c) are included to show the high positive anomaly of ice PSC.

13) P.19, L. 468: The authors claim that "anomalously high PSC areal coverage was observed." However, not reference nor supporting material/figure are shown to support the "anomalously high PSC areal coverage" in 2020. Please show anything to explain that PSC areal coverage in 2020 was anomalously high compare with other years.

Replied under comment #12

< Grammar/Typos >

14) P.2, L.36: Last ";" after Selitto et al. is not needed.

Complied with.

15) P.4, L.120: orbit the Earth ~15 times ---> orbit the Earth ~14 times

The section 2.5 which contains this line is completed removed, as we changed the methodology to retrieve the formation pathways using by studying the temperature history, MLS HNO_3, H_2O along with CLaMS box model simulation of PSC formation.

16) P.6, L.185: $\Delta T = T_n - T_{n+2}$ ---> $\Delta T = T_{n+2} - T_n$

Thank you for pointing out this. The section 2.4 containing this equation no. 3 is completely removed. As we are studying the complete temperature history of the air parcel containing ice/liquid-NAT mixture now (a more vital information than ΔT), we have not considered ΔT in this revised manuscript.

17) P.6, L.186: $\Delta HNO_3 = HNO_{3n} - HNO_{3n+2}$ ---> $\Delta HNO_3 = HNO_{3n+2} - HNO_{3n}$

The section 2.4 containing this equation no. 4 is completely removed. However, we considered the uptake of MLS HNO_3 during PSC formation and compared with CLaMS box model result. This scatter plot of observed MLS HNO3 uptake and CLaMS modelled uptake is shown in Fig. 12 and Fig. 18.

18) P.6, L.188: obtained from MLS and MERRA-2 ---> obtained from MERRA-2 and MLS

Thank you for pointing out. We completely removed section 2.4. This time, we considered temperature from ERA5 operational analysis instead of MERRA-2 as ERA5 is more reliable than MERRA-2.

19) P.9, L.240: in k_{ext} ---> in Δk_{ext}

Complied with.

20) P.9, L.241: the result of mesospheric air ---> the result of the descent of the mesospheric air

Complied with.

21) P.10, L.276: (such as convection or advection. ---> (such as convection or advection).

Complied with.

22) P.10, L.281: chemical production of ---> chemical production or destruction of

Complied with.

23) P.11, L. 298: the same period (Fig. 7a) ---> the same period (Fig. 7c)

Complied with. As the Fig. 1 and Fig. 2 which was demonstrating the methodology which employed to retrieve PSC formation pathways are changed, Fig. 7 became Fig. 5 now. Hence, changed Fig. 7a to Fig. 5c.

24) P.13, L.328: mid-April itself (Fig. 7c) ---> mid-April itself (Fig. 7b)

Complied with.

25) P.15, L.375: ΔHNO_3 = -0.8 ppbv ---> ΔHNO_3 = -1.0 ppbv

The section 3.5.1, which contains this line is removed. However, we presented the change in HNO3 (ΔHNO3) in the form of case studies in revised manuscript. Furthermore, the MLS observed ΔHNO3 is validated against CLaMS modelled ΔHNO3 and shown in Fig. 12 (for liquid-NAT mixture) and Fig. 18 (for ice).

26) P.16, L.399: ΔT = 0.8 K ---> ΔT = 1.0 K

The section 3.5.1 which contains this line is removed.

27) P.18, L.439: ΔT and ΔHNO_3 of -0.7 K, and -0.9 ppbv ---> ΔT and ΔHNO_3 of -1.1 K and -1.1 ppbv

The section 3.5.1 which contains this line is removed.

Author response to Reviewer #3 comments

We sincerely thank the reviewer for the comments and have revised the manuscript thoroughly based on those along with the comments received from other reviewers. 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 #3

The paper by Srinivasan Prasanth and colleagues addresses a very interesting and hot topic: The impact of bushfire events on Antarctic PSC formation, specifically the impact of the extreme Australian bushfire event in 2019/2020 on the occurrence of Antarctic PSC in 2020. The study "aims to investigate the anomalies in stratospheric chemistry and PSC dynamics caused by the Black Summer event" and tries to retrieve and quantify PSC formation pathways.

After reading the manuscript, I came to the conclusion that this study cannot be published. Therefore, my review focuses only on my main concerns along with a few examples.

I have the impression that the authors are newcomers to PSC research. A comprehensive understanding of the cloud formation processes seems to be missing. The data analysis is much too superficial. Averages are given for the whole year, making it difficult to justify the conclusions drawn. I would recommend to take this great data set of CALIOP, MLS and OMPS measurements together with ERA5 data and the CLaMS model and to improve the analysis after an intensive study of the literature.

We appreciate the views of the reviewer on the topic and also on the issues which has been listed in the comments. We have made a careful and thorough revision of our manuscript, based on these comments as well as the comments received from other reviewers and believe that the revision has resulted in improving the scientific content of the paper. Specifically, we have modified the methodology to study the PSC formation pathways and improved the discussion and conclusion section thereafter. All these are incorporated in the revised manuscript (please see also the responses to reviewer #1 in this regard)

In this revised manuscript, to gain information about formation pathways of PSCs, 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, 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, in this revised manuscript, we presented results in the form of case studies along with results from CLaMS box model simulation. To totally 7 case studies are presented:

- Liquid-NAT mixture formation pathways: 2 cases discussing ice-free NAT formation pathway (Case no. 1 at page no. 19 and Case no. 2 at page no. 22) and 2 cases discussing ice-assisted NAT formation pathway (Case no. 3 at page no. 24 and Case no. 4 at page no. 26).

- Ice formation pathways: 2 cases discussing NAT-assisted ice formation pathway (Case no. 5 at page no. 31 and Case no. 6 at page no. 32) and 1 case discussing NAT-free formation pathway (Case no. 7 at page no. 33).

The revised methodology is similar to Nakajima et al., (2016) and Voigt et al., (2018) who 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 given that average cooling rate of the stratosphere. 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 trajectory crosses the CALIPSO scan track within a ±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 is given in Fig. 13 (c) (page no. 29), and for ice in Fig. 19 (page no. 37).

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 are a few selected comments.

Authors should adhere to established PSC terminology. NAT particles are solid and introducing "liquid nitric acid trihydrate (LNAT)" is misleading and won't be accepted by potentially interested readers of this paper. LNAT means that solid NAT particles are mixed with liquid STS droplets.

Thank for pointing out this and we are sorry on this. We have 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

The authors mix the different classification schemes of Pitts et al. The authors use the PSC product v2 (Pitts et al., 2018), but partially describe the classification from the PSC product v1 (Pitts et al., 2009 and 2011).

Thank you for pointing it out and we have corrected this now. Through out the manuscript, now we stick with PSC product v2 classification scheme as described 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

Figure 1: I cannot believe that the scan at 13 UTC on August 01, 2020 shows no PSCs. It is the Antarctic winter. Why should it be a completely different picture 4 hours later? It is also difficult to reproduce the scene because the authors plot the observations with distance on the x-axis. Distance to the intersection? I could not find the LAT/LON coordinates of the intersection point, only the plotted orbits in Figure 1. Figure 2 must be a very small section of the orbits. If these intersections are the basis for the entire PSC formation analysis, I would like to see more examples, broader CALIOP orbits scenes and trajectories connecting the observations.

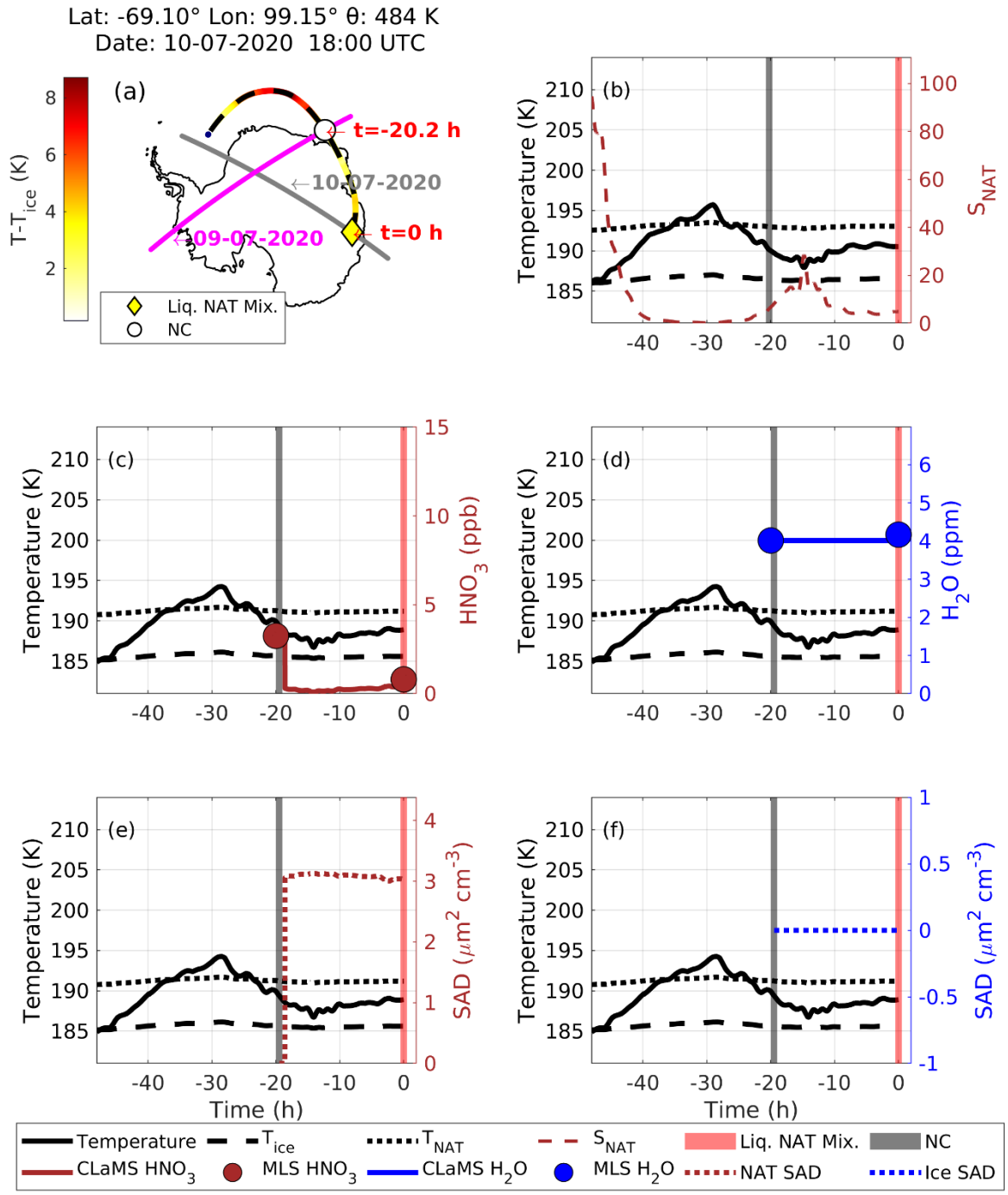


Figure 1. The lagrangian backward trajectory for a 48 h period starting at time, t = 0 h (corresponding to 18:00 UTC 10-07-2020) is shown. Here, the dashed black line is the backward trajectory and the color along this trajectory is the temperature at the T-T_{ice} coordinate. The yellow diamond represents the observed liquid-NAT mixture from the CALIPSO scan track (solid grey line) corresponding to 10-07-2020. The complete coordinate of this liquid-NAT mixture is given in the title. The white circle represents the observed 'No Cloud (NC)' at the time, t = -20.2 h from the CALIPSO scan track (solid magenta line) corresponding to 09-07-2020. (b) shows the saturation ratio over NAT (S_{NAT}) (dashed brown line) and vertical bars mark the liquid-NAT mixture (red) and 'NC' (grey). (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).

We sincerely thank the reviewer for the valuable comment. Following it, we have modified the methodology to retrieve the formation pathways by considering the temperature history of air parcels estimated through Lagrangian backward trajectory along with the MLS HNO_3, and H_2O, and the CLaMS microphysical box model simulation. So, the revised methodology is no longer restricted to the intersection points of two CALIPSO scan track where change in PSC composition is observed as in original manuscript. The approach of retrieving the formation pathway of liquid-NAT mixture is shown here (Figure. 1 in present response). The case study of ice-free NAT nucleation process i.e., NC to liquid-NAT mixture is discussed through Case no. 1 and 2 in the revised manuscript. Here, case no. 2 is briefed below along with plot. In the below case, the trajectory connecting two CALIPSO observation, temperature history (i.e., ambient temperature, T_{NAT}, and Tice), MLS HNO_3, and H_2O at the time of observation of CALIPSO PSC, and corresponding CLaMS box model run are included.

On 10-07-2020, at 18:00 UTC, CALIPSO detected a liquid-NAT mixture at a latitude of -69.1° and longitude of 99.15°, with a potential temperature of 484 K. This observation is marked by a yellow diamond in panel (a) 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).

The backward trajectory reveals that CALIPSO observed 'No Cloud (NC)' along this trajectory 20.2 hours earlier (at the time, t = -20.2 h), on 09-07-2020, marked by a white circle in panel (a). The temperature history shows that between these two observations, the temperature did not decrease below the T_{ice}, indicating that the condition is not conducive for ice formation. At the time of the NC observation, the temperature is ~189 K which is 2 K below the NAT temperature (T_{NAT}). During this time, MLS observed gas-phase HNO_3 and H_2O mixing ratios are 3.5 ppb and 4 ppm, respectively (panel (c) and (d)). Using these as initial conditions, a CLaMS box model run was performed from t = -20.2 h to 0 h, simulating the evolution from the NC to the liquid-NAT mixture. After 20.2 hours, the MLS HNO3 decreased from 3.5 to 0.5 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 3 $\mu m^2\ cm^{-3}$ (panel (e)), while the ice SAD remained at 0 $\mu m^2\ cm^{-3}$, confirming that no ice formation occurred before the observation of the liquid-NAT mixture. During the transition from 'No Cloud' (NC) to the liquid-NAT mixture, the saturation ratio over NAT stayed well below 30, further supporting the absence of ice involvement in the formation of the liquid-NAT mixture (panel b) (Luo et al., 2003; Voigt et al., 2005). It should be noted that, as the liquid-NAT mixture means the mixture of liquid STS and solid NAT, STS PSC should have formed between the observation of NC and liquid-NAT mixture and specifically before the formation of NAT.

Reference:

Luo, B. P., Voigt, C., Fueglistaler, S., & Peter, T. (2003). Extreme NAT supersaturations in mountain wave ice PSCs: A clue to NAT formation. Journal of Geophysical Research: Atmospheres, 108(D15), 4441. https://doi.org/10.1029/2002JD003104

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.

It is impossible to infer anything about PSC formation pathways without looking at individual air parcels and trajectories. The authors use the CLaMS model driven by ERA5 data. This tool provides a high resolution picture of the polar vortex. Instead, the authors use the MERRA temperatures provided with the PSC data, but only at the point of observation. However, it is also necessary to look at the temperature histories along the trajectories between the individual observation points. This is really a key point that I want to emphasize! The authors cannot say anything about PSC formation processes without doing a trajectory analysis.

We sincerely thank the reviewer for the comment and suggestion on studying the temperature histories of air parcels containing air parcels containing PSCs. As suggested by the reviewer, we have replaced MERRA-2 temperature with ERA5 operational analysis temperature. Also, we have calculated backward trajectories for CALIPSO detected ice and liquid-NAT mixture PSCs through CLaMS trajectory module using ERA5 operational analysis meteorological data and studied the temperature histories air parcels along with MLS observed HNO_3, and H_2O. Furthermore, we used CLaMS microphysical box model to gain more insight about the PSC evolution such as ice, and liquid-NAT mixture surface area density. We also validated the MLS observed uptakes of HNO_3, and H_2O gases against CLaMS modelled uptake of these gases.

The formation mechanism of NC -> PSC does not make sense. STS droplets do not form suddenly, they gradually increase in size from the stratospheric sulfuric acid aerosols by taking up HNO3 and H2O and at a certain size they can be detected by CALIOP. Most of the time NAT and ice particles are mixed with STS droplets. Especially when looking at "LNAT". How can LNAT be formed from NC without STS, since LNAT contains STS, otherwise it would not be LNAT?

Yes, we agree that liquid-NAT mixture itself contain the liquid STS. The NAT is liquid-NAT mixture nucleates either on pre-existing ice or on STS with solid foreign nuclei inclusion. Through by saying, 'No Cloud' transformed to 'liquid-NAT mixture, we imply that ice is not involved in formation of NAT i.e., the NAT is formed through ice-free nucleation process. Off course, STS should have formed before NAT formation during observation of 'NC' to 'liquid-NAT mixture transition. To add clarification, now we added this point in page no. 21, L559 to L 561 which is quoted below for quick reference.

"*It should be noted that, as the liquid-NAT mixture means the mixture of liquid STS and solid NAT, STS PSC should have formed between this transition and specifically before the formation of NAT*"

Furthermore, to avoid confusion, we group the liquid-NAT mixture formation pathways into two: ice-assisted nucleation and ice-free nucleation as exists in literature. So, along the backward trajectory of liquid-NAT mixture, if NC/STS are observed along the trajectory and temperature not decreased 1.5 less than T_{ice} (temperature at which ice nucleates heterogeneously), we conclude that liquid-NAT mixture formed via ice-free nucleation pathways. In case, if NC/STS/ice are observed along the pathways, or the temperature of the air parcel decreased 1.5 less than T_{ice}, we conclude that liquid-NAT mixture formed via ice-assisted nucleation pathway.

Another example is here: "If the same air parcel became populated with 'LNAT' after a certain time, this could imply that it formed either by nucleation on stratospheric aerosols favored by the decreased temperature, or by evaporation of large NAT rocks favored by the increased temperature, so that their size now falls within the CALIPSO detection thresholds". NAT rocks may not be detected by CALIOP because of their low number densities. Not because they are too big. As the temperature rises, NAT rocks evaporate and become smaller, but this does not change the number density. They won't be detected just because they're smaller. That makes no sense.

We have corrected these lines and included it in page no. 5 from L158 to L161. The same is given below.

“In addition, gas-phase HNO3 is observed from Microwave Limb Sounder (MLS) during March to April every year. But CALIPSO detects no PSC during the same period. It is due to the sub-visible PSC which are NAT particles with extremely low in number density such that its optical signal is below CALIPSO detection threshold and hence CALIPSO classifies these grids as ‘No Cloud (NC)’ (Lamber et al., 2012).”

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.

“Furthermore, each formation pathway occurs at a specific temperature, which is conventionally viewed in the "T-Tice" temperature coordinate”. This is also far too simplistic. To give just one example, the cooling rate also has an important influence on PSC formation. If the temperature decreases slowly, PSC particles have time to grow. If the temperature decreases rapidly, many more PSC particles can nucleate but remain small. The result and also the PSC class will be different even if the observation point has the same temperature.

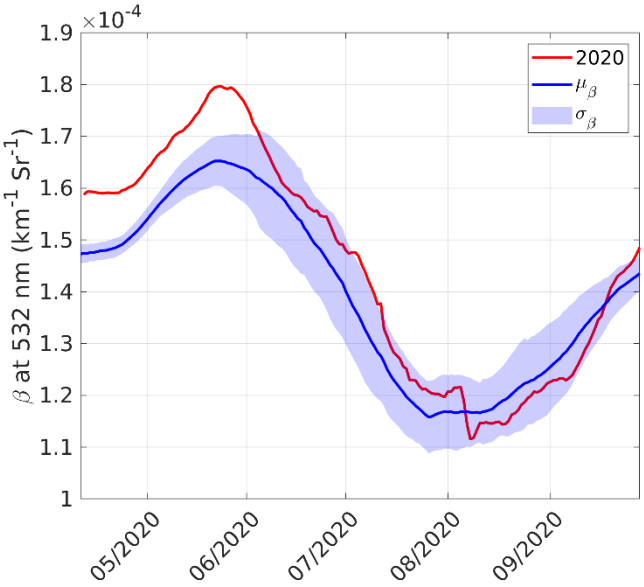
Thank you pointing it out. We understand that temperature history plays crucial role in deciding the PSC class which forms. Hence, we have removed these lines from the manuscript. Furthermore, as per suggestion, we studied the temperature history of air parcels to retrieve the PSC formation pathways as discussed earlier.

How can the authors conclude that "Most of the LNAT (~82%) was formed by heterogeneous nucleation on wildfire aerosols"? They may be able to conclude that NAT formed via a heterogeneous nucleation

pathway. But how do they know that these nuclei all came from the wildfire? Heterogeneous nucleation also occurs in other winters on other foreign nuclei of speculative origin, still a matter of research.

We acknowledge that heterogeneous nucleation of NAT occurs in all winters, and it is not possible to conclude that 'all' liquid-NAT mixture formed through nucleating on bushfire aerosols. We believe that along the foreign nuclei such as meteoritic dust, H2SO4 solid hydrate, bushfire aerosols also could have possibly acted as nuclei and influence PSC occurrence. By analysing temperature history, and presence of PSC along the trajectory, it is possible to conclude whether the NAT nucleating on ice or on STS by Nakajima et al., (2016). Since NAT always nucleates heterogeneously, the STS should be solid foreign nuclei as inclusion. Previous studies shown that these solid foreign nuclei could be the meteoritic dust particle which descent from mesosphere to the lower stratosphere and possibly included in STS droplet. Ansmann et al., (2022) reported that the lower stratospheric aerosol number concentration increased from 10 cm^{-3} (background level) to 100 cm^{-3} based on ground based lidar observation from Neumayer and South pole stations located in Antarctica during 2020. Hence, it is highly likely, together with the background meteoritic dust particles, bushfire aerosol also included into the STS droplet.

To support this, in the first version of manuscript, we shown that the increased stratospheric aerosol loading as observed through Ozone Monitoring Profiler Suite (OMPS) measurement during January-April 2020 is attributable to the intrusion of smoke plumes from black summer event into the lower stratosphere in Fig. 1. As the OMPS does not provide data during polar winter, 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}) which is 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 that bushfire aerosol could have possibly involved in PSC formation process. We believe that along with already existing foreign nuclei such as meteoritic dust particle, bushfire aerosols also infused into STS and acted as nuclei for NAT formation.

Furthermore, in our revised manuscript, the backward trajectories of liquid-NAT mixture revealed that, most of the time no PSCs (i.e. CALIPSO grids classified as 'No Cloud (NC)') are detected by CALIPSO along these trajectories and also temperature have not decreased below T_{ice} (between observation of NC and liquid-NAT mixture), ruling out the possibility of ice formation and thus nucleation of NAT over ice.

Reference:

Ansmann, A., Ohneiser, K., Chudnovsky, A., Knopf, D. A., Eloranta, E. W., Villanueva, D., Seifert, P., Radenz, M., Barja, B., Zamorano, F., Jimenez, C., Engelmann, R., Baars, H., Griesche, H., Hofer, J., Althausen, D., and Wandinger, U.: Ozone depletion in the Arctic and Antarctic stratosphere induced by wildfire smoke, Atmos Chem Phys, 22, 11701–11726, https://doi.org/10.5194/ACP-22-11701-2022, 2022.

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.

Authors response to community comments by Dr. Farahnaz Khosrawi

We sincerely thank Dr. Farahnaz Khosrawi for the valuable comments. Our point-by-point response to the comments are given below. The comments are marked in bold blue font and our responses are marked in normal black font below each comment.

I have read your manuscript with great interest. While reading your manuscript I found several issues that were not clear as well as some technical issues which I provide you here in my comment. I think these will help to improve your manuscript.

Specific comments:

Title: After reading the manuscript I had the feeling that the title does not really fit to the content of the paper.

Thank you for your comment. The main objective of the study is to study the effects of aerosols from the 2019/2020 Australian black summer event on polar stratospheric clouds (PSCs). Our findings reveal that ice PSCs exhibited a significant and anomalous increase in areal coverage. We attribute this to increased stratospheric aerosol loading as revealed by Ozone Monitoring Profiler Suite measurement and by the condensation of HNO_3 on bushfire aerosols forming liquid-NAT mixture, which then rapidly transitioned into ice. Since this result, "enhanced formation of ice PSCs" is central to the paper, we believe the title reflects the most critical finding while remaining concise. We kindly request to retain the current title to highlight this key aspect.

L24: What is LNAT? I have never heard of it. NAT particles are solid particles, so why should these then be liquid? Do you rather mean supercooled ternary solutions?

Thank you for pointing it out. We changed the 'LNAT' to 'liquid-NAT mixture' following the terminology used in Pitts et al., (2018). By LNAT, we meant liquid-NAT mixtures. This is essentially a mixture of liquid supercooled ternary solution and solid NAT.

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

L59: Here you should add "e.g." and also add the references of Khosrawi et al. (2016) and Thölix et al. (2016).

Complied with.

L65: Title of subsection does not fit to the content. In this section also reanalysis data is described. Thus, this subsections should be renamed to "Satellite and reanalysis data"

Thank you for pointing out that. The subsection title is updated now into "Satellite and reanalysis data" at page no. 5, L134.

L119: "…a new methodology" Where is this methodology described? You should provide here a short description of the methodology.

Thank you for the comment. In In this revised manuscript, the methodology is Sect 3.3 from L183 in page no. 6 to L240 in page no. 7. In this methodology, to gain information about formation pathways of PSCs, 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 TNAT 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 TNAT. 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 TNAT.

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 HNO3, and H2O 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 is given in Fig. 13 (c) (page no. 29 in the revised manuscript), and for ice in Fig. 19 (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.

L160: This should rather read "occurrence" than formation.
Complied with.

L167: It is not clear how you get information on the formation pathways. You only get information on the occurrence of PSCs.

In response to the specific comment #5, we briefly described the methodology to retrieve formation pathways of PSC.

L174: Also here it should rather read "occurrence".
Complied with.

L214: It should rather read "chemistry" or "microphysics" than "dynamics".
Thank you for the comment. As there is no any evidence that bushfire aerosols changed the PSC chemistry (for e.g., chemical composition) and microphysical properties such as nucleation or growth rate of PSC. Hence, we would like to choose to use the word 'dynamics' to indicate the overall observed change in PSC, specifically areal coverage of various PSCs as a result of increased HNO_3 and aerosols due to the bushfire event.

L254: There are plenty of references for this statement, thus "e.g." should be added before the reference of Tritscher et al.

Complied with.

L273: References are missing here. There is a special issue on this winter in JGR/GRL and plenty of papers that discuss the vortex dynamics during this winter.

Complied with. We added references for the paper discussing vortex dynamics during 2020 winter at the L404 and L405

L278: Add "e.g." since these two references are not the only ones that could be cited here.

Complied with.

L289: Here ACE-FTS is used, but this data set has not been described in the method section.

Thank you for the comment. The description of ACE-FTS is given in page no. 5 and L144 to L146. The same is quoted here.

"Atmospheric Chemistry Experiment-FTS (ACE-FTS) onboard SciSat satellite provides trace gases mixing ratio by measuring limb absorption spectra and level 2, version 4.0 daily HF, H_2O, HNO_3, N_2O_5 mixing ratio (https://www.frdr-dfdr.ca/repo/dataset/c75d2c49-0def-49e5-9c69-5e74c824dc6c; Bernath et al., 2020) are used in the present study."

L289ff: I still do not understand how to read the correlations. Which part of the correlation refers to chemistry and which to dynamics? Could you mark the respective points in the plot?

Thank you for pointing out. We added a few more points between the L415 and L418 in page no. 14 and paraphrased the Fig. 4 caption in the revised manuscript. Further, we are explaining the same below.

The dynamic and chemical cause for the change in gas composition can be inferred from the scatter plot. For example, the data corresponding during 2020 (red diamond, in Fig. 4(a) in revised manuscript) are much deviated from the regression line made for the background period (blue circle, in Fig. (a)). It suggests that concentration of long-lived chemically inert species, HF does not change during this period. Therefore, the increase in HNO_3 should be due to chemical process. Similarly, during 2020, data corresponding to H_2O (red diamond, in Fig(b)) have not deviated much from the regression line. Hence, it suggests that H_2O is increased due to dynamical cause.

Figure 9 caption: No pathways of formation. To my understanding you solely look at the occurrence of specific PSC types. From CALIPSO data it is only possible to derive information on the occurrence of PSC types, not on the formation pathways. As stated above you have to better explain your methodology.

Thank you for the comment. We agree with the reviewer that CALIPSO provide the information about the PSC occurrence and type but not about the formation pathways. For this reason, we calculated the backward trajectory

analysis of the air parcels containing liquid-NAT mixture and ice PSC to retrieve information about the formation pathways. We added the revised methodology to Sect. 3.3. from L183 in page no. 6 to L240 in page no. 7.

Figure 9 caption: percentage contribution to what? To all particles?

The NAT particle can form either nucleating on pre-existing ice (ice-assisted nucleation process) or on STS with solid foreign nuclei inclusion (ice-free nucleation process). The 'Percentage contribution' says, how much liquid-NAT mixture formed via ice-assisted nucleation process and how much via ice-free nucleation process.

L360ff: Here you mention Tice, but you have nowhere defined/mentioned at which temperatures the respective PSC particles form.

We thank the reviewer for pointing out. These details are added now at L86 to L91.

L381: Isn't that quite logical? Why should it be large NAT if it is obviously no PSC?

When CALIPSO classifies a grid as 'No Cloud', it essentially does not mean there is no physical presence of PSC. As Lambert et al., (2012) (in their subsection 4.2.1) mentioned, as optical properties of large NAT particles (radius > 6 µm) with very 'low number density' falls below the CALIPSO detection threshold, these types of particles are not detected by the CALIPSO but can be detected through HNO_3 depletion from MLS observation. Hence, even if CALIPSO classifies certain grid as 'No Cloud', it essentially does not mean there is no PSC but corresponds to NAT with low number density and large size.

Lambert, A., Santee, M. L., Wu, D. L., & Chae, J. H. (2012). A-train CALIOP and MLS observations of early winter Antarctic polar stratospheric clouds and nitric acid in 2008. Atmospheric Chemistry and Physics, 12(6), 2899–2931. https://doi.org/10.5194/ACP-12-2899-2012

L397: This is pure speculation. You cannot derive from your analysis any conclusions on the formation process, i.e. if it was homogeneous or heterogeneous.

As per the revised methodology, as brief in response to specific comment #5, we study the temperature history of the air parcel. Based on that, and also type of PSC which observed along the backward trajectory of the liquid-NAT mixture, we group the liquid-NAT mixture formation pathways into two: ice-assisted nucleation and ice-free nucleation as exists in literature. So, along the backward trajectory of liquid-NAT mixture, if NC/STS are observed along the trajectory and temperature not decreased 1.5 less than T_{ice} (temperature at which ice nucleates heterogeneously), we conclude that liquid-NAT mixture formed via ice-free nucleation pathways. In case, if NC/STS/ice are observed along the pathways, or the temperature of the air parcel decreased 1.5 less than T_{ice}, we conclude that liquid-NAT mixture formed via ice-assisted nucleation pathway.

L392: What about temperature fluctuations induced by waves? These are not resolved by the reanalysis data.

We acknowledge the view with thanks. We agree that ERA5 data does not resolve small scall fluctuation. For this reason, we are not discussing the formation of mountain wave induced ice, and enhanced NAT in the present study.

L411: I don't think that the solid kernel of a PSC can be detected by a lidar. They usually detect if the particle is generally liquid or solid. With their schemes they can characterize the type of PSC (NAT; ice is STS), but not if in the formation a foreign nuclei was involved.

Thank you for the comment. We understand that CALIPSO provides just PSC composition/type only but not formation process. Using the methodology which we described in subsection 2.3.1 in original manuscript, we noticed a few STS changed to liquid-NAT mixtures. This transition is possible if NAT is nucleated on the STS. Hanson and Ravishankara (1991; 1992) have shown through laboratory experiment that homogeneous nucleation of NAT on STS (i.e., STS without any foreign nuclei inclusion) is less likely for stratospheric condition. Furthermore, in general, homogeneous nucleation of NAT is kinetically suppressed as shown in Koop et al., (1995). Hence, it is highly probable that during the STS to liquid-NAT mixtures transition, NAT nucleated heterogeneously on STS (i.e., STS with solid nuclei).

Hanson, D. R. and Ravishankara, A. R.: The reaction probabilities of ClONO2 and N2O5 on 40 to 75% sulfuric acid solutions, Journal of Geophysical Research: Atmospheres, 96, 17307–17314, https://doi.org/10.1029/91JD01750, 1991.

Hanson, D. R. and Ravishankara, A. R.: Investigation of the reactive and nonreactive processes involving nitryl hypochlorite and hydrogen chloride on water and nitric acid doped ice, J Phys Chem, 96, 2682–2691, 1992.

Koop, T., Biermann, U. M., Raber, W., Luo, B. P., Crutzen, P. J., and Peter, T.: Do stratospheric aerosol droplets freeze above the ice frost point?, Geophys Res Lett, 22, 917–920, https://doi.org/10.1029/95GL00814, 1995.

L432: No, there could be temperature fluctuations by waves which are not resolved by the meteorological analysis.

We agree with the reviewer's view that small scale fluctuation by waves are not resolved in ERA5 reanalysis. Hence, we are not discussing the influence of the small scale temperature fluctuation on PSC formation pathways.

L444: As stated above. From lidar you cannot get any information in the nucleation process. Only information on the type (composition) of a PSC can be derived.

We agree with the view that CALIPSO provides just the information of PSC's presence and type, but not formation pathway. In response to the specific #5, we brief the methodology to retrieve the formation pathway. Please also kindly see the detailed the revised methodology added in the revised manuscript at Sect. 3.3. from L183 in page no. 6 to L240 in page no. 7.

L450: This is a contradiction. Why is it called liquid NAT if it is solid?

To avoid confusion, we changed the terminology 'LNAT' into 'liquid-NAT mixtures' as in Pitts et al., 2018. The liquid-NAT mixture is mixture of liquid-STS and solid NAT.

L469: chemistry should be replaced by composition since PSCs are not formed by chemistry.

Complied with.

L471: As also already stated above, the methodology has not been clearly explained and this needs to be improved to make this study more convincing.

In response to the specific #5, we brief the methodology to retrieve the formation pathway. Please also see the detailed the revised methodology added in the revised manuscript at Sect. 3.3. from L183 in page no. 6 to L240 in page no. 7.

L473: This is only speculation. I do not see any proof in your analysis for this.

Thank you for the comment. In response to the specific comment #5, we brief the revised methodology to formation pathways. Using that, in the revised manuscript, we discussed the formation pathway of ice and liquid-NAT mixture. Here, we discuss one of the cases briefly.

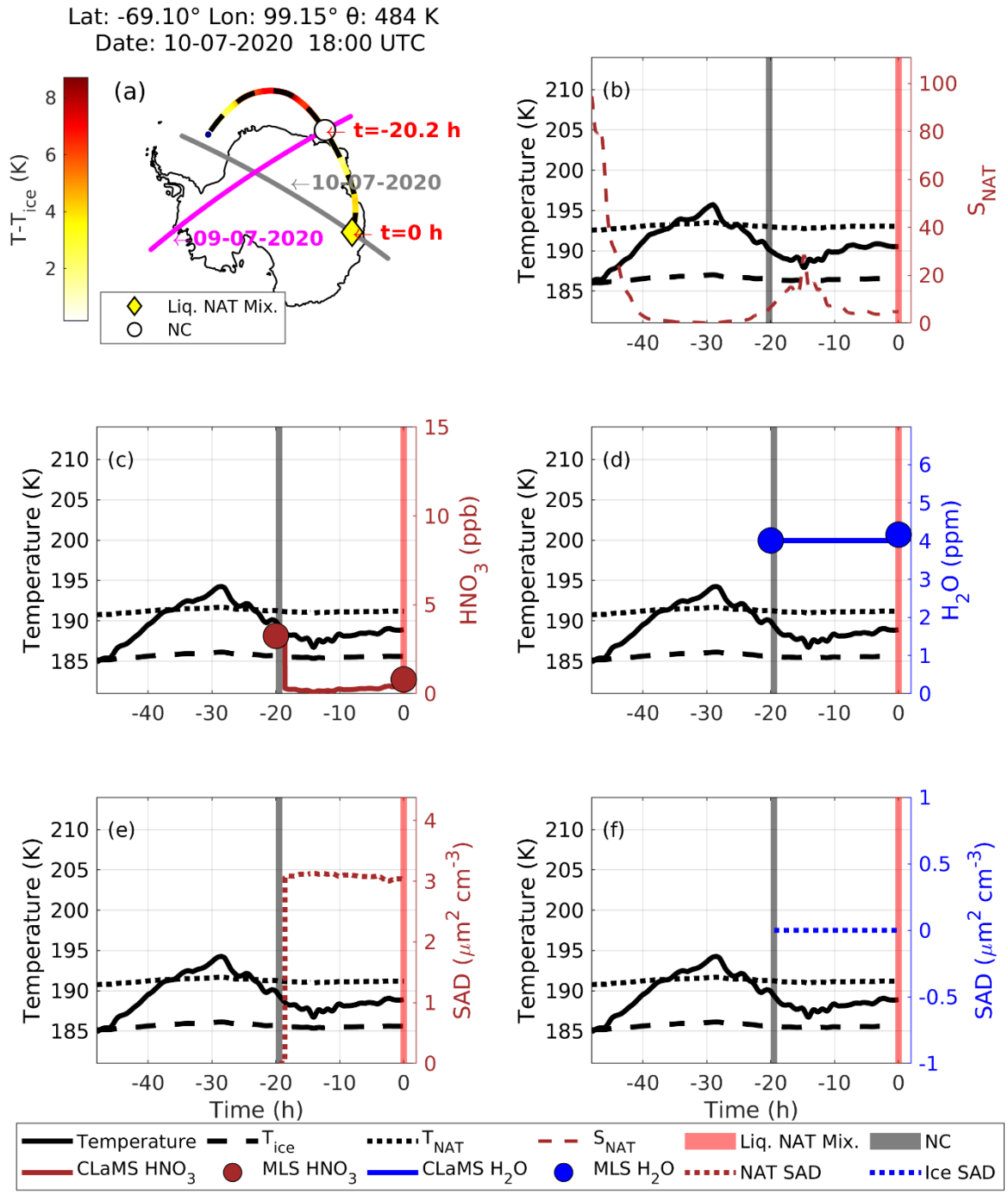


Figure 1. The lagrangian backward trajectory for a 48 h period starting at time, t = 0 h (corresponding to 18:00 UTC 10-07-2020) is shown. Here, the dashed black line is the backward trajectory and the color along this trajectory is the temperature at the T-Tice coordinate. The yellow diamond represents the observed liquid-NAT mixture from the CALIPSO scan track (solid grey line) corresponding to 10-07-2020. The complete coordinate of this liquid-NAT mixture is given in the title. The white circle represents the observed 'No Cloud (NC)' at the time, t = -20.2 h from the CALIPSO scan track (solid magenta line) corresponding to 09-07-2020. (b) shows the saturation ratio over NAT (S_{NAT}) (dashed brown line) and vertical bars mark the liquid-NAT mixture (red) and 'NC' (grey). (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 H2O, and the solid blue line represents the CLaMS H2O. (e) shows the NAT

surface area density (SAD) (dotted brown line). Panel (f) shows the ice surface area density (SAD) (dotted blue line).

On 10-07-2020, at 18:00 UTC, CALIPSO detected a liquid-NAT mixture at a latitude of -69.1° and longitude of 99.15°, with a potential temperature of 484 K. This observation is marked by a yellow diamond in panel (a) 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).

The backward trajectory reveals that CALIPSO observed 'No Cloud (NC)' along this trajectory 20.2 hours earlier (at the time, t = -20.2 h), on 09-07-2020, marked by a white circle in panel (a). The temperature history shows that between these two observations, the temperature did not decrease below the T_{ice}, indicating that the condition is not conducive for ice formation. At the time of the NC observation, the temperature is ~189 K which is 2 K below the NAT temperature (T_{NAT}). During this time, MLS observed gas-phase HNO_3 and H_2O mixing ratios are 3.5 ppb and 4 ppm, respectively (panel (c) and (d)). Using these as initial conditions, a CLaMS box model run was performed from t = -20.2 h to 0 h, simulating the evolution from the NC to the liquid-NAT mixture. After 20.2 hours, the MLS HNO3 decreased from 3.5 to 0.5 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 3 $\mu m^2\ cm^{-3}$ (panel (e)), while the ice SAD remained at 0 $\mu m^2\ cm^{-3}$, confirming that no ice formation occurred before the observation of the liquid-NAT mixture. During the transition from 'No Cloud' (NC) to the liquid-NAT mixture, the saturation ratio over NAT stayed well below 30, further supporting the absence of ice involvement in the formation of the liquid-NAT mixture (panel b) (Luo et al., 2003; Voigt et al., 2005). It should be noted that, as the liquid-NAT mixture means the mixture of liquid STS and solid NAT, STS PSC should have formed between the observation of NC and liquid-NAT mixture and specifically before the formation of NAT.

L480: Stratospheric chemistry not shown and discussed in this study. However, a changed PSC occurrence will definitely affect stratospheric chemistry.

Thank you for the comment. We discussed the change in stratospheric trace gases in subsection 3.2, and their cause in subsection 3.3. The subsequent subsections discuss the influence of these changes on PSC occurrence. However, the change in stratospheric chemistry due to the change in PSC occurrence is not discussed. We acknowledge the reviewer view on this, and it will be helpful to extend the study in future.

L487: Based on which measurements?

Using Microwave Limb Sounder (MLS) measurement. We added this information in the L1085.

L491ff: High HNO3 and H2O and aerosol are not the sole reason for enhanced PSC occurrence. Also the temperatures need to be sufficiently cold. Was this a cold or warm winter? Other studies have not shown any influence so far.

We agree that temperature also needs to be sufficiently cold for enhanced PSC occurrence. But Fig. 3d and Fig. 4d show that, there is no significant negative temperature anomaly for 2020 winter i.e., the temperature during this period is comparable to the background period (2012-2019). But strong positive anomaly in HNO_3, and aerosol is observed. Hence, it is likely that increased HNO_3, and aerosols are primary reasons for enhanced PSC occurrence.

L494: You cannot make any statements on the formation mechanism. This is only guessing and should be more carefully expressed.

We understand the concern regarding the formation pathways retrieval. We revised the methodology and strengthened the discussion section to support the findings. Please kindly see the revised methodology section 3.3.

Technical corrections:

L36: Semicolon between "2020" and closing parenthesis obsolete.

Complied with.

L41: add "in the abundance" (or "the amount") so that it reads "changes in the abundance of various trace gas species".

Complied with.

L44: rephrase sentence.

Complied with.

L54: paramount -> change wording

Complied with.

L71: trace gases mixing ratio -> trace gas mixing ratios

Complied with.

L73: add "s" -> mixing ratios

Complied with.

L225: to the -> to a

Complied with.

L271: tracer-trace -> tracer-tracer

Complied with.

L276: Tracer-Tracer -> Tracer-tracer

Complied with.

L279 and 280: tracer gas -> trace gas

Complied with.

L285: Tracer-Trace -> Tracer-tracer

Complied with.

L312: and aerosol aging -> and "the" aerosol "ages" or "is aging".

Complied with.

L317: by -> to

Complied with.

L321: and discussed -> and is discussed

Complied with.

L317: add "on sulfate aerosols" so that it reads "results in the condensation of these trace gases on sulfate aerosols".

Thank you for the suggestion. We changed the L457 to "results in the condensation of these trace gases on stratospheric aerosols" as the condensation of the trace gases are not limited to the sulfate aerosols but also on other aerosols like meteoritic dust, volcanic ash, soot, or H_2SO_4 hydrates.

Figure 8 caption: Move "monthly mean" before "areal coverage" so that it reads "monthly mean areal coverage" or better write directly "monthly averaged areal coverage".

Complied with.

Figure 10 caption: redline -> red line

Complied with.

L497: anticipated -> expected

Complied with.

References:

Khosrawi, F., Urban, J., Lossow, S., Stiller, G., Weigel, K., Braesicke, P., Pitts, M. C., Rozanov, A., Burrows, J. P., and Murtagh, D.: Sensitivity of polar stratospheric cloud formation to changes in water vapour and temperature, Atmos. Chem. Phys., 16, 101–121, https://doi.org/10.5194/acp-16-101-2016, 2016.

Thölix, L., Backman, L., Kivi, R., and Karpechko, A. Yu.: Variability of water vapour in the Arctic stratosphere, Atmos. Chem. Phys., 16, 4307–4321, https://doi.org/10.5194/acp-16-4307-2016, 2016.