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.

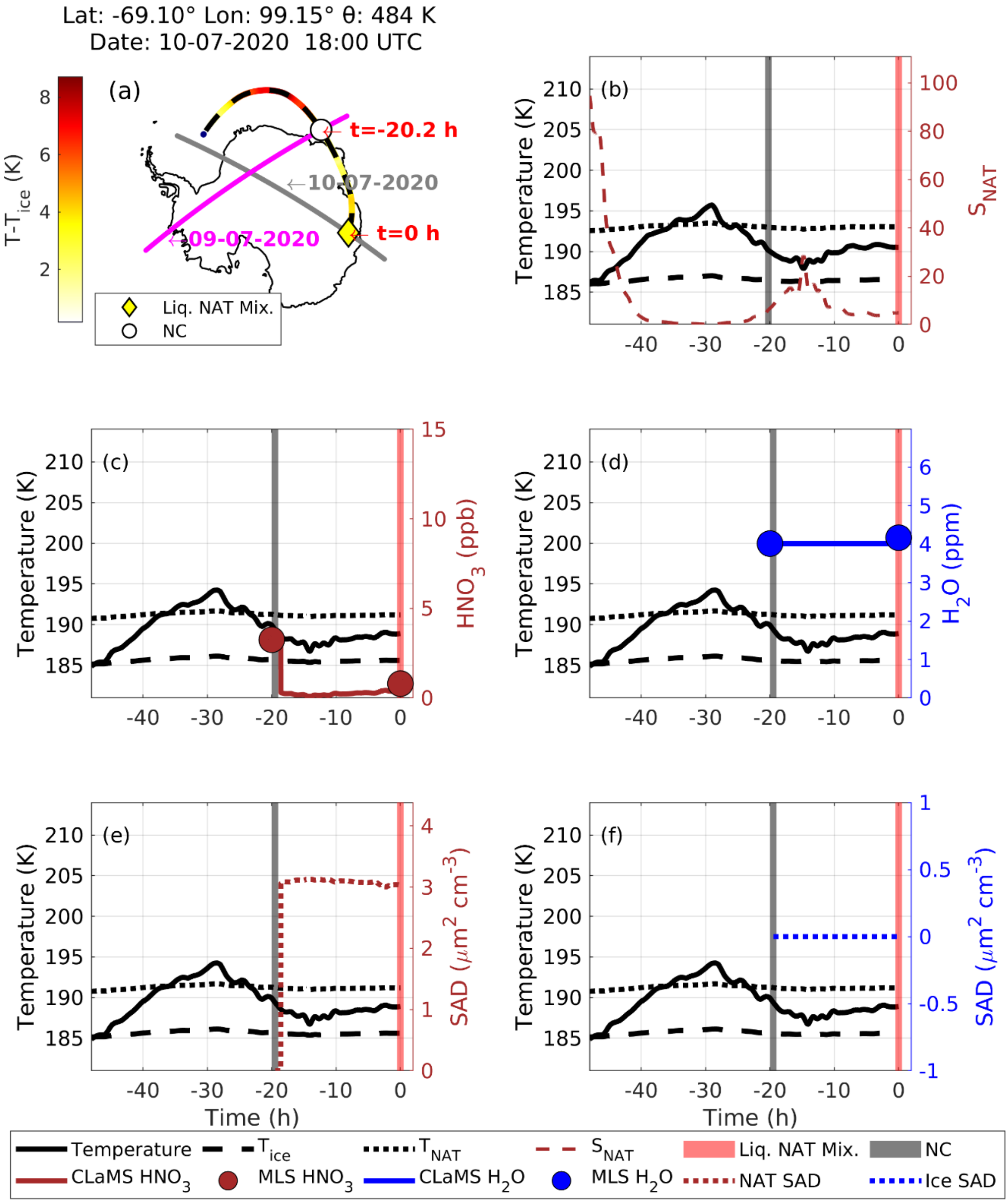


Figure 1. The lagrangian backward trajectory for a 48 h period starting at time, t = 0 h (corresponding to 18:00 UTC 10-07-2020) is shown. Here, the dashed black line is the backward trajectory and the color along this trajectory is the temperature at the T-T_{ice} coordinate. The yellow diamond represents 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.

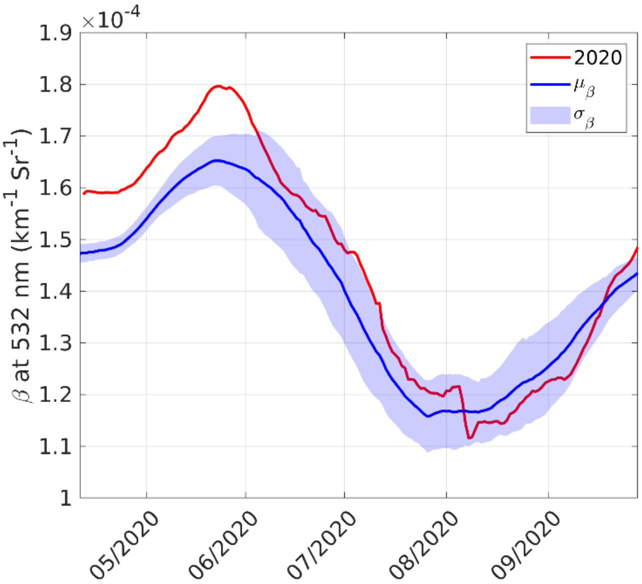
Thank you pointing it out. We understand that temperature history plays crucial role in deciding the PSC class which forms. Hence, we have removed these lines from the manuscript. Furthermore, as per suggestion, we studied the temperature history of air parcels to retrieve the PSC formation pathways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