

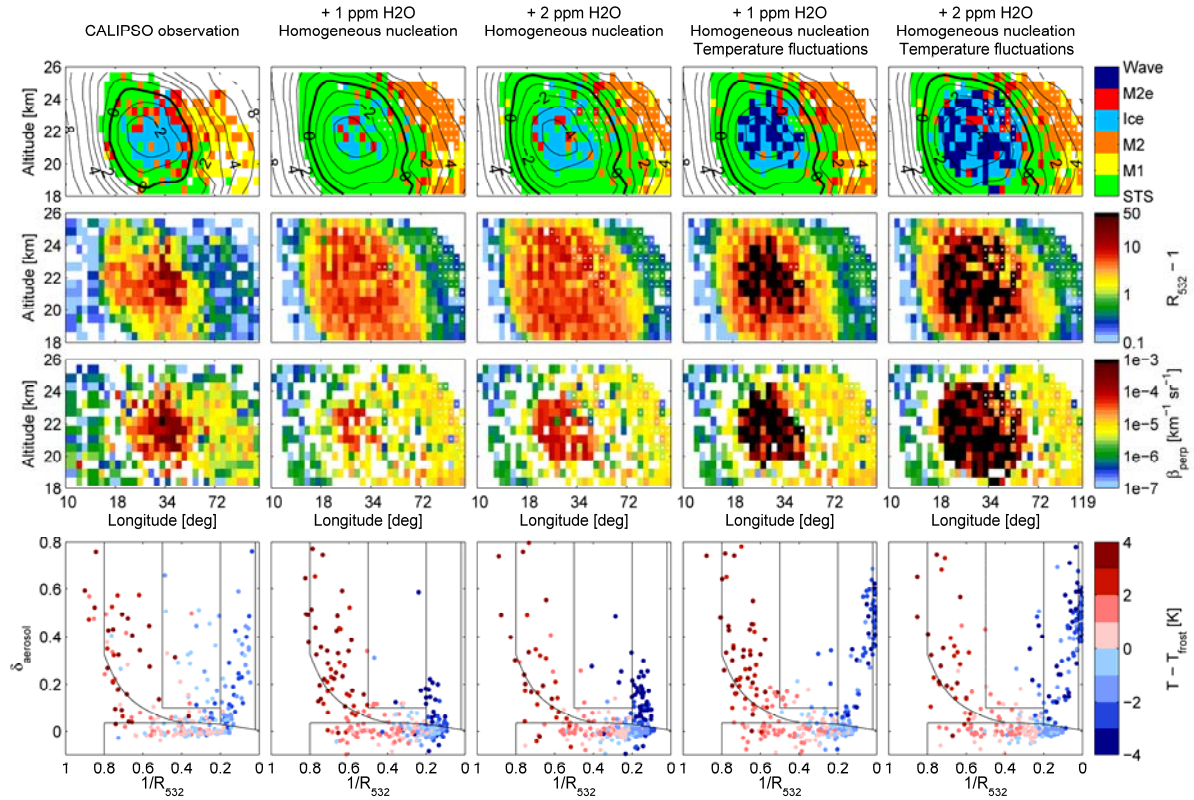
We would like to thank the anonymous reviewer for reading this manuscript and offering suggestions for improvements. In the following, we respond to his/her comments.

1. *Please tone down hyperbole ('unprecedented' in the abstract) and be more circumspect in your conclusions so as to be more consistent and considerate of your (relatively limited) experimental design. There are large uncertainties in your methods, despite your presenting a relatively compelling story and narrative. In particular, your lack of constraint for H<sub>2</sub>O and HNO<sub>3</sub> mixing ratios is very concerning. MLS is coarse, and your interpolation schemes even coarser. My estimates say that the uncertainties in your frost point estimates likely exceed 2 K, which is enough to weaken many of your claims (you should be more forthright about these uncertainties). Additionally, given the recent Nature paper by Anderson et al. (2012), and the potential enhancement of NH water vapor from increased overshooting midlatitude convection, the uncertainties in H<sub>2</sub>O are potentially very large. Back trajectories, particularly in the lower stratosphere, are further limited by uncertainty. I'm not generally questioning the veracity or fidelity of your claims and conclusions, but I don't think should be accompanied by such bold claims as 'unprecedented'.*

We follow the Reviewer's suggestion and on the one hand replaced the word "unprecedented" in the abstract by "compelling" and on the other hand broadened the discussion about uncertainties in our method. For this, we added the following information to page 8838, line 8:

"This modeling approach relies on temperature information obtained from output from the ERA-Interim reanalysis produced by the ECMWF, which assimilates meteorological measurements. Furthermore, MLS measurements hold uncertainties in the gas phase H<sub>2</sub>O and HNO<sub>3</sub> mixing ratios, which affect the calculations of  $T_{\text{frost}}$  and  $T_{\text{NAT}}$ . Typical single-profile precisions are 4 to 15 % for H<sub>2</sub>O (Read et al., 2007; Lambert et al., 2007) and 0.7 ppbv for HNO<sub>3</sub> (Santee et al., 2007). The daily vortex-averaged data used here are not able to fully resolve fine-scale structures. Therefore, the data may under or over-estimate local maxima or minima, which would also change  $T_{\text{frost}}$ . An underestimation of the water vapor mixing ratio by 1 ppm would increase  $T_{\text{frost}}$  by roughly 1 K."

Enhancements in the stratospheric water vapor concentrations, as reported by Anderson et al. (2012), should be visible in the Aura MLS data. However, the coarse vertical resolution and the use of daily mean vortex averaged values contribute to the uncertainties in our study. To demonstrate the effect of a 1 and 2 ppm change in H<sub>2</sub>O on  $T_{\text{frost}}$  and ice formation (which would roughly be comparable to a 5 and 10 ppb change in HNO<sub>3</sub> with respect to  $T_{\text{NAT}}$ ), we performed four additional model runs, which exclude heterogeneous ice nucleation. Results are presented in the figure following this paragraph. An increase of 2 ppm H<sub>2</sub>O (3rd column) could indeed quantitatively counteract heterogeneous ice nucleation. The area filled by synoptic-scale ice is comparable to the observations (1st column), but simulated values of depolarization stay below the observations. Adding temperature fluctuations produces wave ice (4th and 5th column) for the same reason as explained in the publication. A reduction of the fluctuation amplitude or the possibility of heterogeneous ice nucleation with a re-tuned parameterization might lead to a satisfying agreement. However, we rate a permanent underestimation of 2 ppm in H<sub>2</sub>O as unlikely and, as visible in the following figure, an agreement with the measurements requires more than homogeneous ice nucleation on synoptic-scale trajectories.



2. I'm having difficulty reconciling the claim that "This is in contradiction to our previous laboratory-based understanding of NAT formation, which (1) excluded the possibility homogeneous NAT formation" with the model of Tabazadeh et al. (1994 - GRL) that seemingly opens the possibility for this path.

Nucleation rates measured by Koop et al. (1995) and Knopf et al. (2002) conclusively show that homogeneous nucleation of NAT cannot explain observed NAT number densities in the order of  $10^{-4} \text{ cm}^{-3}$ . Knopf et al. (2002) reported NAT number densities less than  $5 \times 10^{-7} \text{ cm}^{-3}$  from experimental data under the assumption that PSC particle formation takes place for two months at measured rates (please see also the answer to Comment 2 from Reviewer 1).

3. It would be useful for the reader to justify your claim that ice nucleates homogeneously only when  $T \leq T_{\text{frost}} - 3 \text{ K}$ , as I believe that you are attributing this to the rate of necessary vapor supersaturation. Its best clarified for the reader.

As suggested also by Reviewer 1, we added the citation of Koop et al. (2000), which states that the nucleation rate coefficient is dependent on the ice saturation ratio and the supersaturation necessary for homogeneous ice nucleation is reached at approximately  $T < T_{\text{frost}} - 3 \text{ K}$ . We clarified this for the reader.

4. Your reconciliation of meteoric materials as the source of heterogeneous ice nuclei (btw, please be clear and up front that you are discussing contact nucleation almost exclusively...it comes out later in Sec. 2.3.1, but was unclear my first go through the text) is fairly unconvincing. Its mostly hand waving to suggest that your model parameterizations seem most in line with observations and then use words like "likely" in the abstract. Can you change that to "plausibly" to be more neutral (again, that word circumspect)? In fact, in the conclusions, the narrative is more circumspect on this point. Food for thought, I'm frankly very interested in the impact that pyrocumulonimbus residues have on background stratospheric aerosol particle fields (non-volcanic). Surely, biomass burning materials aren't as efficient as active ice nuclei as other materials, but you guys make some assumptions about the distribution of the background composition that doesn't necessarily consider active perturbations like PyroCB (see Fromm et al., 2010 BAMS).

(1) The heterogeneous NAT and ice nucleation pathways on foreign nuclei implemented in our microphysical model take place in the immersion mode, not contact mode. We assume that foreign nuclei are immersed in the background aerosol. We realized that this is not clearly stated in our manuscript and therefore added this information on page 8835, line 13: "In the immersion mode, we adopt the functional dependence of nucleation on active sites..." We also emphasized the immersion mode in Section 2.3.1 and changed "nucleation starting as soon as the vapor is saturated" on page 8841, line 7 into "nucleation starting as soon as supersaturation is reached".

Additionally, we clarified this in Fig. 1. We improved Fig. 1 by (1) highlighting that NAT and ice nucleation takes place in an immersion mode (therefore we encircled the black triangle, which represents the foreign nuclei) and (2) replaced "Ice + NAT + STS" in the lower right corner by "Ice + NAT + SBS". After nucleation of NAT or ice, an SBS and not an STS coating is present on the particle.

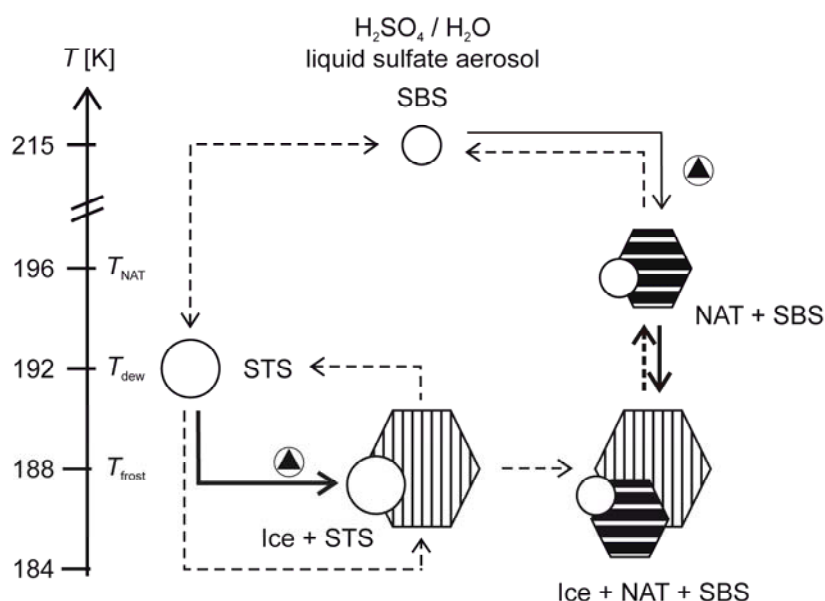


Fig. 1: PSC formation pathways implemented into ZOMM (Zurich Optical and Microphysical box Model) with SBS = Supercooled Binary Solution ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ), STS = Supercooled Ternary Solution ( $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ), NAT = Nitric Acid Trihydrate ( $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ ),  $\Delta$  = foreign nuclei, e.g. meteoritic dust, immersed in STS aerosol droplets (surrounded by circle). Dashed arrows denote pathways included in previous schemes (e.g. following Lowe and MacKenzie, 2008; Peter, 1997). Solid arrows show the heterogeneous nucleation pathways of NAT and ice on preexisting solid particles supported by the new field observations. Thick arrows are discussed within this publication; thin solid arrow is discussed in companion paper (Hoyle et al., 2013). Note that some arrows are unidirectional (i.e. the other direction is thermodynamically not possible), while others are bidirectional.

- (2) We would like to point you to our answer given to Comment 1 from Reviewer 1 for a discussion about the choice of number densities, sizes and composition of the foreign nuclei. From our study, we can neither confirm nor exclude sources like volcanoes or pyroCb injections instead of or in addition to meteoritic material. A detailed chemical analysis of the refractory aerosol material from RECONCILE particle samples revealed that also crustal material and anthropogenic sources contribute to the chemical composition of the material (von Hobe et al., 2013). However, since those kinds of measurements are missing along the trajectories and, moreover, we don't know the nucleation ability of different kinds of foreign nuclei, we can only indirectly account for this in our parameterization. As discussed in Hoyle et al. (2013) a change in number densities and/or composition of available foreign nuclei would simply force us to re-tune our parameterizations and not change our conclusions.

5. *I'd like to see your conclusions broadened. Where are you going with this work? What is the significance of heterogeneous nucleation being potentially dominant relative to homogeneous? How does this effect potential and future parameterizations in your model? Ultimately, what is the point? This is very good paper, and you guys just sorta let it die when you should seemingly have so much more to say about impact and future directions.*

We extended our conclusion by adding the following paragraph at the very end:

“Tabulated NAT and ice nucleation rates can be derived from the present work, which allows straightforward implementation of the new parameterization into large scale models. Such an approach reflects the nucleation process far more realistically than current methods involving constant nucleation rates. The use of the new parameterization in three dimensional models, such as in the recent CLaMS study (Grooß et al. 2013, ACPD) should lead to improved representation of dehydration and denitrification and thus better simulations of ozone loss.”

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