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Interactive comment on "Nitric acid trihydrate (NAT) formation at low NAT supersaturations" *by* C. Voigt et al.

Anonymous Referee #2

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This paper details a new set of measurements of NAT particles which make an important contribution to the PSC literature. First, these are the first measurements of "young NAT rocks", i.e. NAT particles with small concentrations, but with much smaller sizes than previously observed by Fahey et al. [2001] and Northway et al. [2002]. Second, these measurements provide the most unambiguous evidence to date that NAT particles first form in air that has only experienced moderate NAT saturation ratios (S_{NAT}<11). As discussed in the paper, the existence of these particles provides a strong constraint on the freezing processes which are responsible for solid-phase PSC formation.

The paper also provides interesting speculation on the role of meteoritic particles in

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causing heterogeneous freezing. This section of the paper makes several interesting points, in particular that the laboratory measurements of Biermann et al. [1996] only rule out rapid heterogeneous freezing (at the time, NAT clouds were assumed to contain large concentrations of NAT particles). However, these measurements may still be consistent with the much slower freezing necessary to explain very small concentrations of NAT particles now known to exist in the stratosphere.

However, the section on heterogeneous freezing contains a few misconceptions that should be fixed. Most importantly, the authors vascillate between two concepts of how heterogeneous freezing occurs. One concept is that heterogeneous freezing is rapid, and solid-particle concentrations are limited by few nuclei. For example, on p. 8592 they state that "Obviously potent nuclei must be available with sufficiently low surface areas". Then on p. 8595 they state that "the nucleation process acts like a switch and all available nuclei may be activated within a small temperature range". However, the meteoritic freezing process that they explore is conceptually very different: a very slow heterogeneous freezing process (freezing timescale of more than one year), which is only able to have an effect because of the relatively large meteoritic surface area (and the small NAT concentrations needed). These nuclei are not "potent" and the freezing process does not act "like a switch", and therefore directly contradict the author's above-quoted statements. Section 6.5 in particular is marred by the incorrect assumptions about the nature of heterogeneous freezing, and needs to be revised.

Specific comments:

title: needs to specify the paper is about atmospheric observations, i.e. "Stratospheric observations of nitric acid trihydrate ..."

p. 8584, ln 11: "enhanced fluctations" How large are these fluctuations compared to instrument noise?

p. 8584, ln 14: in calculating T_{NAT}, is HNO_3 assumed to be 100% of NO_y ?

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p. 8555: In section 4.1, it would be useful to provide the inferred HNO_3 content (ppbv) of the NAT particles, in addition to the provided size distribution information. The omission is especially noticeable given that the ppbv of HNO_3 in the liquid particles is provided for both time periods. Furthermore, the relevance of the liquid phase HNO_3 is questionable. Not only is 0.03-0.04 ppbv well below the stated 0.3 ppbv detection limit, it is likely to be sampled in both the forward-facing and rear-facing inlets (i.e., the HNO_3 is in particles smaller than 0.2 μm) and therefore does not contribute to ΔNO_y.

p. 8586, ln 8: "is less than 1.5%" Provide details on the derivation of this number (or appropriate reference).

p. 8587, ln 6: "reach the ice frost point" NAT particle growth is reduced before the ice frost point is reached, since ternary solution growth becomes significant above the ice frost point

p. 8587, ln 17-18: provide the actual value used for the NAT nucleation rate (3.e-9 $cm^{-3}s^{-1}$?)

p. 8587, ln 28: Clarify whether the DLAPSE model simply shows existence of PSCs in a single grid box. Is the model resolution 2.8x2.8? It seems that any difference in areal extent between the model and measurements can probably be attributed just to the difference in resolution.

p. 8588, ln 3-4: Change to "the particle nucleation process *presumably* depends on..." Clarify the meaning of "variations of the air masses".

p. 8588, ln. 5-6: "an increase ... could explain those discrepancies" Given that no calculations to support this point have been done, "might" would be more appropriate than "could"

p. 8588, section 4.4: This section could be strengthened by emphasizing that these NAT particles, containing very little HNO_3 and with small concentrations, are in fact not detectable with most existing instrumentation. Not only does this underline the unique

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capability of in-situ NO_y instrumentation, it also provides a context for the paucity of previous measurements of such particles: these particles are not necessarily rare, just hard to measure.

p. 8590, p. 20: Include that Gross et al. conclude best case is 3.4e-6 $cm^{-3}h^{-1}$

p. 8591, ln 26: Is Figure 5 the correct reference?

p. 8592, ln 2: "Summarized NAT sedimentation" What is meant by summarized?

p. 8594, lns 1-5: The statement that "Biermann et al. (1996) found that the presence of meteoritic material accelerates the freezing ..." needs to be qualified, especially since the title of the paper is "The Unsuitability of Meteoritic and Other Nuclei ..." Some of the material at the end of the page (lns 23-25) needs to be introduced here, explaining why the authors are re-interpreting the original results. Provide more details on the experiment, for example the time scales necessary for a test tube to freeze even with meteoritic material, and the statistics required to infer a freezing rate from a single sample. A reference to Bogdan et al. [2003] would also be appropriate.

p. 8594, ln 4: The provided freezing rate is not for S_{NAT} = 20. This freezing rate corresponds to the "best case" in Biermann et al. [1996], which was 5 min time period for freezing, in solution 5. In solution 2, the time period was 100 min, i.e. a freezing rate 20 times slower, although it is easy to overinterpret the differences between the cases when only one data point exists for each solution.

p. 8594, ln 16: "must be regarded as a possible pathway" This statement is an overstatement. Heterogeneous freezing perhaps "must" be regarded as a possible pathway, but the role of meteoritic particles remains speculative

p. 8594, lns 19-21: More than just 3 days below T_{NAT} is necessary to explain the Fahey et al. [2001] observations. Although perhaps sufficient to explain the slightly larger concentrations, the more important difference in the Fahey data is the large particle sizes which require up to 6 days below T_{NAT}.

p. 8595, ln 25: Did the model calculations truly use 8.e-6 as the nucleation rate? The discussion on p. 8587 implies a rate closer to 1.2e-5.

Figure 1: show the T_{NAT} contour

Figure 4: Clarify whether gas-phase HNO_3 is assumed to be constant during the simulation, i.e. whether the NAT particle concentration is presumed to be so small that NAT does not approach equilibrium.

Figure 5: The different line widths used for the gray and red lines (or at least shown in the legend) introduces some confusion. In particular, it is not clear whether the gray ensemble is truly colder than the red trajectories during the final ten hours, or is it just a graphics artifact? Also, this figure could possibly be more instructive if the PSC ensemble was compared specifically to trajectories generated along sections of the Geophysica flight path in which no PSCs were seen, rather than to trajectories for which there is no information on the presence/absence of PSCs. Finally, a better label is needed to replace "ECMWF white area".

References:

Bogdan, A. et al., Study of finely divided aqueous systems as an aid to understanding the formation mechanism of polar stratospheric clouds: Case of HNO3/H2O and H2SO4/H2O systems, J. Geophys. Res., 108, 4302, doi: 10.1029/2002JD002605, 2003.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 8579, 2004.