

Interactive comment on “Ice condensation on sulfuric acid tetrahydrate: implications for polar stratospheric ice clouds” by T. J. Fortin et al.

Anonymous Referee #3

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The authors present a study of heterogeneous ice nucleation on sulfuric acid tetrahydrate (SAT), which may be important for Polar Stratospheric Clouds. The laboratory study is complemented with model calculations to estimate the impact of this ice nucleation mechanism on the dehydration of the polar vortex. They find that ice nucleation on SAT requires a supercooling of 0.1–1.3 K under polar stratospheric conditions, which is considerably lower than the supercooling required for homogeneous nucleation (2.5–3K). This implies that ice clouds may form more often than previously thought.

Apart from minor corrections/suggestions given in 'Varia' at the end, there are two aspects of the paper which require a serious revision before the paper is acceptable for ACP. The problems are the stratospheric relevance of the suggested mechanism and the modeling of dehydration.

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1. Stratospheric relevance:

The authors point out that 'sulfate aerosols can and do, on occasion, exist in a frozen state.' (p4) With reference to Gable et al. [1950] the authors write that SAT is the thermodynamically stable form of frozen sulfate aerosol. However, they do not mention at all that 'stratospheric conditions' implies also HNO₃ (with concentrations of 10 ppb) in the gas phase. It is well known that the presence of HNO₃ alters the thermodynamic properties of SAT. I agree with the authors that there may be SAT in the polar stratosphere (in particular Beyerle [2001] seems to make a strong point), however there is no direct evidence yet, and I do not accept the sentence that SAT 'can, and do ...', but require that the authors write that SAT *could* exist in the polar stratosphere. Furthermore, the sparse observations that support the SAT hypothesis do not allow to estimate the frequency of occurrence of the SAT particles. The few observations that support SAT in Beyerle et al. and other references despite a huge dataset seem to suggest that SAT, if it really is SAT, is rare, rather than ubiquitous in the polar stratosphere. The authors are also requested to replace 'on occasion' with a more precise term.

Apart from the fact that the occurrence of SAT in the polar stratosphere is not well established, I am not convinced by the paper that ice nucleates on SAT under stratospheric conditions. The authors do not cite two references which must be cited and discussed in this context: Koop and Carslaw, Science, 1996, and Iraci, Fortin and Tolbert, JGR, 1998 (their own work!). Koop and Carslaw (henceforth KC) show that the presence of HNO₃ significantly alters the behaviour of SAT. In particular, they show that the SAT deliquescence point is above the ice frost/melting point in the presence of HNO₃ (see Figure 2 of KC). The vortex must be extremely denitrified for the SAT deliquescence temperature to be lower than the ice melting temperature (see Figure 2 of KC, assume 5ppmv for H₂O, p = 50hPa, which yields an ice melting point of approx. 188.5 K. The SAT deliquescence temperature is only for less than 2 ppmv HNO₃ close to or below the ice melting temperature. I do not know of any measurement that ever reported such low HNO₃ mixing ratios from Arctic measurements, not even from

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Antarctic measurements). The Iraci/Fortin/Tolbert (henceforth IFT) paper reports the same behaviour, and even suggests that NAT could form in the liquid ternary film that formed on the SAT surface.

The authors are requested to address this issue in the revised version.

2. Modeling of dehydration:

The final particle number density of an ice PSC depends strongly on the cooling rate, the number density of the heterogenous condensation nuclei (SAT in this case) and the number density of the liquid particles which may freeze homogeneously. Dehydration, in turn, strongly depends on particle number density of the ice particles. The sedimentation velocity is roughly proportional to the square of the particle radius, and if too many particles have to share the available water from the gas phase they will remain too small to efficiently sediment (Jensen et al., Impact of polar stratospheric cloud particle composition, number density, and lifetime on denitrification, *J. Geophys. Res.* 107 (D20), 2002, discuss this for denitrification and could be used as a reference). It thus surprises that the cooling rates of the trajectories are not discussed at all. A global model such as UKMO may not only have a bias in absolute temperature (as described), but certainly has a bias towards moderate cooling rates due to the limited spatial and temporal resolution (mesoscale perturbations cannot be fully resolved). I consider a discussion of this issue absolutely central to any modelling of dehydration. Given the possibility of stronger cooling rates, homogeneous nucleation may outrun heterogeneous nucleation, rendering the impact of SAT on dehydration much smaller. Also, it is not obvious as to why the authors consider SAT particle number density in the range $1\text{E-}5$ to $1\text{ cm-}3$. Why not $10\text{ cm-}3$, approximately the number density of the sulfuric acid background aerosol? Do the authors assume a mechanism that selects only a fraction of the liquid background aerosol to become (remain?) SAT? The authors do not compare the modelled dehydration with measurements, although they refer to the measurements of Hermann et al. and Schiller et al.. In Drdla et al. [2003] it is stated the the simulated dehydration exceeds the measured values. I assume this to

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be even more true when heterogeneous nuclei lower the nucleation barrier, unless the number density of the ice particles is larger than 1 cm^{-3} (which is also apparent in Fig. 8). I think the authors should compare the new values with their own work (Drdla et al.). To summarize, I suspect that the modelled dehydration exceeds the measured dehydration due to the inaccuracy of the cooling rates of the trajectories. Given this uncertainty, the provided simulations cannot help to answer the important question whether ice nucleation on SAT (if it occurs at all) is of importance to the dehydration of the polar vortex.

3. Varia:

Section: Abstract

Sentence: 'In the model simulations, even a very small number of SAT particles (e.g. $1\text{E-}4 \text{ cm}^{-3}$) ...'

Apart from the discussion of cooling rates given earlier, I think this is not quite consistent with the caption in Figure 8, that says that results with $1\text{E-}5 \text{ cm}^{-3}$ SAT are indistinguishable from a simulation without SAT. Rather, it appears to me when looking at Figure 8 that $n > 1\text{E-}3 \text{ cm}^{-3}$ has an impact on dehydration which could be mentioned in the abstract.

Section: Results and Discussion

Given that the SAT deliquescence temperature is close to the ice melting temperature (even in the absence of HNO_3), the reader might wonder whether the observed ice nucleation may take place on a liquid film rather than on the 'dry' SAT surface, particularly when taking into account the required supersaturation with respect to ice (S-ice) of up to 1.3. If this were the case, it would of course render the discussion of 'm' useless. From a back-of-the-envelope calculation I think that this is not the case (maybe you can also outrule this possibility from the observed spectra?), but it would be useful to have this information at hand, e.g. plot a line in Figure 5a that shows the supersatura-

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tion with respect to ice necessary for SAT deliquescence.

Section: Atmospheric Implications

As stated before, I do not trust the authors' calculation of dehydration. Apart from this, I recommend that the authors describe the model in more detail. It is clear that the model is already described in Drdla et al. [2003], nonetheless the reader should be given a bit more information (for example how the authors are able to calculate dehydration with a lagrangian box model). Please describe also briefly the characteristics of the UKMO model (spatial and temporal resolution of wind/temperature fields used for the calculation of the trajectories).

p14, l7: The observed dehydration was small, please give numbers instead of '... some dehydration ...'.

p14, last line, Figure 7b: I assume that the constant value for the mixing ratio of H₂O leads to the black points in Fig. 7b above T-ice, whereas the model dehydrates/rehydrates. Please comment this briefly.

p. 15, l16/17: Why is the dehydration associated with ice nucleation on SAT less intense than for homogeneous freezing?

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 867, 2003.

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