

***Interactive comment on “Ice supersaturations exceeding 100% at the cold tropical tropopause: implications for cirrus formation and dehydration” by E. Jensen et al.***

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The paper is concerned with the interpretation of aircraft measurements of relative humidity over ice at the cold tropical tropopause. In the campaign under consideration (Pre-AVE), exceptionally high values have been measured that deserve special attention. This work adds to recent publications dealing with similar measurements (albeit lacking relative humidities over ice above 170% or so) carried out at middle latitudes. High supersaturations in the TTL and the relationship to the onset of ice formation are climatically relevant.

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The paper is generally well written; exciting observations are described and attempts are made to interpret the findings. The paper concludes by delineating consequences for freeze-drying processes near the cold point tropopause, if the Pre-AVE observations would apply generally in the TTL. Publication in ACP is clearly warranted, but I have a number of points which should be addressed in the discussion stage.

#### 1. Interpretation of laboratory measurements of homogeneous freezing

The authors compare the measurements of Koop et al. (2000) with in situ measurements. The laboratory measurements are not only based on sulfuric acid particles, as suggested on p.7435 (lines 22–25), but on 17 further species, including organic solutions, many of which are of atmospheric relevance. This should be clarified in the introduction.

In these laboratory measurements, the freezing particles were in equilibrium with ambient water vapor at any given temperature. They provided ice saturation ratios where homogeneous freezing commences, not the peak ice saturation ratios achieved in an ice-forming air parcel. The final parameterization of the homogeneous nucleation rate coefficient provided by Koop et al. (2000) depends on the aerosol water activity (not ambient relative humidity). This allows non-equilibrium effects to be taken into account in microphysical model applications. Was water activity used to calculate freezing rates in the calculations shown in Figures 2–4 or was the freezing rate of each particle evaluated at the ambient water saturation ratio? This should be clearly stated, as explained next.

In interpreting detailed measurements of homogeneous ice formation, Haag et al. (2003) (see their Figure 11) explained that at low temperatures (190–195 K) and a cooling rate of 6 K/h, the onset of homogeneous freezing was delayed over the equilibrium prediction by 8% or more in terms of relative humidity over ice, because the first freezing aerosol particles lag behind equilibrium due to slow diffusion of water molecules to the droplets. While cooling rates might have been slower during the Pre-

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AVE observations, temperatures have been several degrees lower, so I would expect a similar effect in the field observations. If the authors made an equilibrium assumption in their simulations underlying Figures 2–4, they would be unable to reproduce this effect.

In this regard, it is misleading to plot the equilibrium results of Koop et al. (2000) directly into Figure 1. These values may not be directly comparable because of non-equilibrium effects of water uptake and – in addition – a possibly substantial difference between the ice saturation ratio where freezing commences and the peak ice saturation ratio achieved in the parcel (the latter is 4% in the model of Haag et al. (2003), Figure 11). I suggest to at least discuss these issues very early in the paper and to add bars to the Koop equilibrium curves shown in Figure 1, indicating how large peak ice saturation ratios might actually get including kinetic effects. I presume the difference between these values and the observations then decreases.

Further paragraphs to be modified along these lines include p.7438 (line 11); p.7439f (lines 23ff and 1ff); p.7450 (lines 1–3).

## 2. Chemical composition of supercooled aerosols

The authors emphasize that the measurements give no evidence of an unusual aerosol composition in the supersaturated air sampled (p.7442, lines 17+18; p.7444, lines 1–7). It is suggested that the freezing particles were mostly composed of organics and sulfates. I can agree with the latter, but not with the former statement, and I think that this issue deserves a more detailed discussion in the paper.

Neither the particulate organic compounds have been chemically specified nor the sulfate-to-organics ratio in different particles have been identified. As both have been shown to affect homogeneous ice formation (Cziczo et al., 2004; Kärcher and Koop, 2004 hereafter KK04). I argue that too little information is available to state whether the aerosol probed during Pre-AVE was or was not different from other TTL aerosol measurements in terms of their ice formation capability.

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The KK04 study separates two effects by which organics internally mixed with sulfuric acid affect the homogeneous freezing. First, miscible organics could decrease the hygroscopicity of pure sulfuric acid, which causes particles to condense less water prior to freezing. The resulting smaller sizes of these organic-rich particles causes delayed or suppressed freezing compared to organic-poor particles. Second, in addition to this thermodynamic effect, the water mass accommodation coefficient could be altered by organic compounds, especially when they act as surfactants. Low values (way below 0.1) of this coefficient would lead to a similar delay of homogeneous freezing, as also shown in the present discussion paper.

The simulations described on p.7444 (lines 8–26) thus confirm a similar approach presented by KK04, which should be properly cited. The mass accommodation effect is then described on p.7444f (lines 27ff), confirming the basic conclusions of KK04 that organic-rich aerosols might lead to enhanced peak ice saturation ratios and total ice crystal number densities. Obviously, a model was used here that tracks water activity in individual particles to produce Figure 5 (see statement p.7445 lines 14–18). It is perhaps worth noting that the inferred reduction of mass accommodation could be smaller when at the same time organics are allowed to dissolve in the bulk aerosol particles and render them less hygroscopic.

### 3. Water saturation and plausibility of relative humidity measurements

The paper discusses uncertainties in determining the saturation vapor pressure of pure water often needed to derive the homogeneous freezing conditions. This is clearly a viable point to make. In view of the very high observed ice saturation ratio near 2.3, it would be worth noting at which value current best estimate of the water vapor pressure (Murphy and Koop, 2004) liquid water would be saturated at 187 K. Once water droplets form, there is no doubt that they immediately freeze and rapidly deplete gaseous water. This may provide information on which values of ice saturation ratio (observed maxima  $>2$  according to Figure 1) can be considered realistic.

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#### 4. Frequency of occurrence of high ice supersaturations

The paper makes a good point of mentioning that the high ice supersaturations are reached only transiently (p.7447, lines 22–26; p.7448, lines 18–25). This puts the measurements into perspective and nicely relates to previous studies showing that frequency distributions of relative humidity in supersaturated regions fall off quasi-exponentially (e.g., Kärcher and Haag, 2004). Numerical simulations, including those by the first author, do allow for supersaturation in cirrus, but mean values are certainly found at moderate supersaturations. I would suggest to highlight this view at more prominent places in the paper, e.g., in the conclusions and perhaps introduction or abstract.

#### 5. Other comments

p.7435, line 19

You might add after "... lower supersaturations" before the citation: "but would not very often prevent homogeneous freezing to occur in the TTL close to the cold point". I would then start a new paragraph, which should be modified in view of issue 1 above.

It may be a matter of taste, but I would finally shift the paragraph starting p.7435 line 28 ending p.7436 line 6 up to p.7435 line 14 to discuss in situ observations together.

p.7438, lines 13–19

Does this hold when a model is used that considers the actual water activity in particles during freezing? The non-equilibrium model of Haag et al. (2003) does predict a notable difference, as noted in issue 1 above.

p.7447, line 17 – p.7448, line 3

The described effect on water vapor concentrations (and the sensitivity with regard to cloud cover) is very similar to the effects of heterogeneous ice nuclei in the TTL. You might wish to mention Kärcher (2004) here as this study is already cited.

p.7450, lines 1–3

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I do not think that water was in equilibrium with the aerosols in the low temperature AIDA experiments, recall issue 1 above.

p.7452, line 8  
nuclei (typo)

p.7454, line 22  
Meteorol. Z.

#### References

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