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Interactive comment on "The role of organic aerosols in homogeneous ice formation" *by* B. Kärcher and T. Koop

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We are pleased that reviewer 2 generally regards our work as well written and useful and like to provide answers to the few issues raised in the report below.

General comment

It is criticized that we leave open what the basis was for chosing the size distribution of particles used in the simulations. The mean lognormal mode radius (0.1μm) and width (1.5) are chosen such that most of the freezing particles are in the accumulation mode size range. This choice takes into account that atmospheric particles which have been chemically analyzed (e.g., with the PALMS instrument) are 0.1–1μm in size. Much larger liquid particles do hardly exist in notable concentrations in the upper troposphere, while an aged accumulation mode is always present prior to cirrus cloud formation (e.g., Schröder et al., 2000). Smaller Aitken mode particles only have a chance to freeze homogeneously when this reservoir of larger particles is depleted. We are taking a lower limit concentration of free and upper tropospheric accumulation mode particles (typically several 100 cm^{-3}), but observe in our calculations that crystal number densities are typically only a fraction of the total aerosol, consistent with observations. We will include part of this text on p.6722 after line 12 in the revision.

Our statement about the lack of sufficient observations being a problem for modellers is termed odd by the reviewer. We presume that he/she refers to p.6733 lines 6–9 in our paper. We do think that this is true, because the modeling community is unable to make robust predictions of cloud formation without sound knowledge of basic facts and also because improved measurements could hardly be designed. However, we also believe that the reviewer's suggestion (our study indicating the need for more specific data) is true. Although our above cited statement implicitly contains this suggestion, we will spell it out explicitly on p.6735, line 19: ”Our study further indicates the strong need for more specific data, because current ...”. The line ”Here we touch a general problem:" will be deleted.

Finally, we do consider at least one aspect of phase change issues on p.6736 lines 1–5; see the comment on this point later in our reply (see point 5.a).

Specific comments

1. Abstract

We agree with the referee that it is unknown whether malonic acid is a prominent organic component in upper tropospheric aerosols. However, as noted in the answer to referee 1, we believe it to be a good surrogate for the water uptake behavior of aerosols containing organics in general. We will add a section explaining in more detail our motivation for choosing malonic acid and include data from the literature on the water uptake behavior of other organic acids to put our choice into perspective.

2. Microphysical model
The water-activity-based nucleation model does not require the knowledge of ice–solution surface tensions. It is clear that organics in aerosols can have an impact on the gas-solution surface tension, and this affects water uptake on organic aerosols via the Kelvin effect in our approach. This will be clarified both on p.6722 and on p.6731.

We neither fail to consider associated uncertainties in our results nor judge this issue unimportant, as our discussion of Figure 4 on p.6731 lines 3–8 reveals. In fact, we point our that only at low T and very low α begin uncertainties in calculating the Kelvin correction to the solution vapor pressure to affect our results.

3. Deposition coefficient
We do not see which of the issues summarized in the Conclusions would change in principle by lowering the deposition coefficient. Its main effect would be to increase the peak ice saturation ratios and the total ice crystal concentrations over those discussed here. Also, exceptionally low values for the water vapor deposition coefficient on ice would contradict recent field (Kärcher and Ström, 2003) and laboratory measurements (Haag et al., 2003).

To satisfy the reviewer's concern, we will address this point on p.6722 by pointing this out and noting the value of the ice deposition coefficient we have used in the model (0.5).

4. Speculations concerning high observed ice supersaturations
Our simulations show (Figure 3) that S_i values up to 1.8 could be approached when only few organic-containing particles characterized by low accomodation coefficients α are available for homogeneous freezing. The purpose of mentioning temperature fluctuations and vapor pressure uncertainties was to list possible additional – not alternative – mechanisms which might have affected recent field measurements of ice saturation ratios S_i left unconsidered here.

We have related this discussion to observations made during CRYSTAL-FACE of peak

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S_i values of 1.8. We do not claim that such high values are caused by small-scale temperature fluctuations alone, but argue that this could generally increase peak values by about 0.05–0.1, depending on the amount of ice present and on T. The impact of the pure water vapor pressure is more difficult to estimate as it is not well known at low T, but associated errors could easily change S_i in the 0.1–0.2 region. In the revised text, we add these numbers to put associated changes of peak S_i into perspective.

We clarify the intention of this paragraph by incorporating these points into the text on p.6733.

It is clear from our work (and from one review, see Kärcher (2004)) that we support Jensen et al. (2004) in that organic particles with low α could have played an important role in creating high ice saturation ratios observed during pre-AVE; these high values are not widespread but represent only a small subset of the data.

5. Conclusions

a. We agree with the referee that there exist several possibilities of how a partial crystallization in aerosol particles might affect their freezing.

First, as mentioned in the manuscript on p.6736, the freezing mode might change from homogeneous to heterogeneous. The precipitated crystal, possibly an organic solid, might induce heterogeneous nucleation at the liquid/solid interface. Such processes have been observed to occur in pure ammonium sulfate particles in laboratory experiments. Alternatively, ice nucleation in the deposition mode at the gas/solid interface might occur. These heterogeneous nucleation processes are likely to depend not only on the type of precipitate, but also on the morphology of the crystals. Modeling such processes would be highly speculative, since no information on heterogeneous ice nucleation rate coefficients under such conditions are available at present for any organic crystal.

Secondly, as mentioned by Referee 2, homogeneous ice nucleation might be ham-

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pered in partially or fully crystallized particles. This would be the case, if the deliquescence relative humidity for the precipitate is larger than the relative humidity required for homogeneous ice nucleation of the fully liquid, but otherwise identical, particle. For partially crystallized particles, the reduced liquid volume would lead to a reduction in the actual nucleation rate, and for fully crystallized particles, homogeneous nucleation would be switched off entirely. However, the latter case requires efflorescence of all individual solute species in a single aerosol particle. This appears to be somewhat unlikely when several solute species are involved, since the deliquescence relative humidity will also be reduced considerably (see, e.g., Marcolli et al., 2004). We will include a brief discussion of this possibility in the conclusion section.

To summarize this point: when compared to homogeneous ice freezing of fully liquid aerosols, partial crystallization of aerosol particles, if it occurs, will most likely complicate modeling the ice freezing of aerosol due to additional processes, either by promoting heterogeneous ice nucleation or by reducing homogeneous ice nucleation. To our opinion, these additional complications, together with uncertainties due to the lack of laboratory data, would justify to investigate this topic in a separate study on its own. In our present study, we focussed on the case of homogeneous ice nucleation in fully liquid particles. With our model we can show that even for this most simple case preferential ice nucleation might occur.

This discussion will be added to p.6736 after line 5.

b. Sentence will be removed.

c. Nowhere in the text we claim that our work is comprehensive. We state the limitations of our approach and spell out conceivable uncertainties. Possibly the reviewer mixed up our term ”convenient" (which we now skip) on p.6736 line 12 with ”comprehensive".

We do not like to mix up phenomena related to phase changes with the homogeneous freezing issue (recall the title of this paper). This would justify a study on its own, which, however, would be highly speculative at this point, see the discussion above under point 5a . One would be forced to keep deliquescence relative humidities and solid-liquid nucleation rates as open parameters. We will slightly modify the last paragraph lines 12–15 to emphasize that homogeneous ice formation is the main concern of our study.

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