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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Efficiency of immersion mode ice nucleation on surrogates of mineral dust" *by* C. Marcolli et al.

C. Marcolli et al.

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We thank reviewer 1 for his/her thoughtful comments.

Detailed response to reviewer:

I agree to referee 2 that the authors should comment on the possibility of lanolin getting to the dust/water interface and thereby influencing the IN activity.

Response: We discuss this in the revised manuscript (see response to reviewer 2).

Section 2.3 Particle size distribution: How do these size distributions of the dry dispersed ATD samples compare to those in the suspensions with water? Particles could stick together in a different way in the wet suspension (see also page 9698, line 3 and following).

Response: Conglomeration of mineral dust in the wet suspension leads to a lower effective number of particles per ATD mass. For a given ATD concentration, the number of particles and therefore also the number of emulsion droplets filled with ATD will be lower. This would increase the ratio between homogeneous/heterogeneous freezing peaks in the DSC thermogram. Because the modeled curves represent this ratio well, we conclude that the ATD particle size distribution determined on a dry dispersed ATD sample is also valid in the wet suspension.

p.9695, l.16: The statement about particle size and curvatures only holds for the mineral particle as a whole, but what if the nucleation sizes are related to surface roughness structure which may have dimensions and curvatures well in the range of the critical nucleation germ sizes? This needs to be mentioned here at least as a possible source of uncertainty or even limitation for the idealized concept of contact angles which may in general be questioned as an appropriate model for heterogeneous ice nucleation by inhomogeneous substrates like mineral surfaces.

Response: We use the contact angle as a fitting parameter. We did not want to evoke a microscopic picture of ice nucleation with this.

However, I do not in general question here the concept of combining a model for heterogeneous surface nucleation rates with some surface dependent probability distribution of nucleation sites with different activation thresholds. I just believe that the surface site distribution, in this work nicely introduced and treated as a variation of the contact angle together with the probability distribution of active sites scaled to the particle surfaces, is the key parameter here. In other words, the results support the so-called singular hypothesis for heterogeneous ice nucleation, as clearly mentioned in the discussion section. The time dependence introduced by the surface nucleation rate seems to appear on shorter time scales (because of the steep relationship between the nucleation rate and the temperature) and may actually not be visible on the time scales the DSC experiments are sensitive to. Would the authors agree that a temperature and surface area dependent activation threshold distribution alone would be sufficient to explain

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and fit the experimental results, without any introduction of a time-dependent surface nucleation rate?

Response: We do not fully agree with the last sentence. Its validity depends on the variation of cooling rates that is considered. If we compare the cycles run at 1 and 10 K/min, the freezing onsets shift to 1.5 - 2.2 K lower temperatures for the cycles run at 10 K/min. If the cooling rates were varied by several orders of magnitude the time dependence would indeed become important.

I would like to add that the probability distribution of surface sites may not necessarily scale to the particle surface. If the most active sites are for instance related to the surface roughness the smallest particles may actually have a higher surface density of defects and therefore active sites because the ATD sample used for the experiments is a ground sample. The mineralogical composition which probably influences the nucleation activity may also vary with particles size. These factors should at least be mentioned in the discussion section as further contribution to the complexity and uncertainty in explaining and formulating heterogeneous ice nucleation by mineral particles.

Response: In this study, we applied the active site parameterization to two size-distributions which were quite similar and therefore did not provide a rigorous test of the postulated size dependence. For a stricter validation, freezing experiments on size-selected ATD samples are needed. We will mention this in the revised manuscript.

Here I would like to add that I do not agree to the statement by U. Schurath made in an open discussion contribution that this work is the first to demonstrate that heterogeneous ice nucleation on substrates like minerals occurs on surface sites with a large range of activation energies. Already Anderson and Hallett (J. Atmos. Sci, 822, 1976) have clearly shown and discussed this behaviour for different materials and it was also demonstrated and discussed in experimental work by Knopf et al. (J. Geophys. Res. 111, D12201, doi:10.1029/2005JD006894, 2006) and Möhler et al. (Atmos. Chem.

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Phys. 6, 3007, 2006) that mineral particles exhibit a range of activation sites with different activation thresholds, though for the deposition nucleation on mineral particles at lower temperatures. Archuleta et al. (Atmos. Chem. Phys. 5, 2617, 2005) also mentioned in their conclusions that active sites may by important. The authors of the present paper already referred to the work by Knopf et al. (2006) and Möhler et al. (2006) in the discussion section and may decide to additionally refer to Anderson and Hallett (1976) and Archuleta et al. (2005).

Response: We mention these studies now in the conclusions of the revised manuscript.

p.9696, l.7 to 25: What about temperature gradients within the DSC emulsions? The arguments used for the estimate of the heat transfer time scale seem to assume homogeneous temperature distribution. Is this a reasonable assumption?

Response: The fact that we can reproduce the observed freezing peaks by our model gives us confidence that our model assumptions cover the relevant heating effects.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9687, 2007.