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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous freezing of droplets with immersed mineral dust particles – measurements and parameterization" *by* D. Niedermeier et al.

Anonymous Referee #2

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This paper addresses the important issue of heterogeneous ice nucleation in mixed-phase clouds and the related question how heterogeneous ice nucleation can at best be formulated as a function of aerosol properties. The Leipzig Aerosol Cloud Interaction Simulator LACIS was used for the ice nucleation measurements and classical nucleation theory was applied to interpret and discuss the experimental results in a broader context. Though the paper provides a description of a new and promising experimental setup for ice nucleation studies and discusses interesting new results in terms of coating effects on heterogeneous ice nucleation of mineral particles, I recommend major revision along the questions and comments listed below before the paper can be accepted for publication in ACP.

Major concerns: The manuscript gives, as far as I can see, no information at all about the actual temperature and humidity profiles the dust particles experience in the nucleation sections. This information is a prerequisite for e.g. judging the applicability and suitability of classical nucleation theory (CNT) for data evaluation and interpretation. Also, what about radial temperature and humidity gradients in the aerosol center flow? Is the temperature known at the saturation point? In other words, is the temperature range known the droplets are exposed to?

And what about the nucleation time? Was the nucleation time varied to prove that a stochastic nucleation rate approach, i.e. a time dependent formulation appropriate to fit the experimental data? Such an approach implies that the nucleation conditions, here mainly the temperature, stay constant throughout the nucleation time period with a constant formation rate of ice. This obviously is not the case in the LACIS setup. Instead the droplets form at some temperature and are further cooled to the temperature which is taken as the supercooling or freezing temperature in the manuscript. What if a significant fraction of ice is already formed or nucleated during this 'cooling path'? Can this really be excluded? If not the CNT approach would only provide lower limits of the nucleation rate.

As far as I see the CNT analysis as used by the authors also assumes that all particles have the same probability to carry active sites for heterogeneous ice nucleation. Is this a reasonable assumption for mineral particles? The particle and generation procedures are only uniform with respect to particle mobility size and probably also coating layers. But the aerosol is still a complex mixture with respect to e.g. mineralogy and surface morphology. Therefore it can be assumed that not only one surface site but a mixture of different sites with different activation energies (or contact angles) are present in the aerosol. A larger fraction of ice particles observed at lower T may also be interpreted partly by a larger number fraction of aerosol particles to carry sites with higher activation energy and therefore lower activation temperature (singular hypothesis). Both the time dependent and singular hypothesis approaches can be found in the recent lit-

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erature to evaluate and parameterise laboratory measurements of heterogeneous ice nucleation (see e.g. Marcolli et al., ACP, 7, 5081, 2007 or Connolly et al., ACP, 9, 2805, 2009), and it is not yet clear which one applies best or if a mixture of both should be used. I think that LACIS is a promising new setup to gain such information just by systematically varying particle sizes, number concentrations and nucleation times. Unfortunately, the manuscript in its current version lacks of such information. Therefore the experimental data seem to be over-interpreted in terms of conclusions for CNT parameterisation and I recommend the authors to be more careful with statements about the comparability with or between other measurements (e.g. on page 15831, lines 3 to 8 or page 15846, lines 22 to 26).

Also it is not clear how the authors can exclude contributions from deposition nucleation. This question may sensitively depend on the temperature at the condensation point. It is known from many literature studies that dust particles can be active deposition mode nuclei, though normally at lower temperature compared to freezing modes. Figure 4 indicates ice formation before droplet activation occurs in the first cooling ramp. I would suspect that the uncoated and slightly coated cases are affected by deposition nucleation, whereas the thicker coatings suppress deposition mode IN but still allow the freezing modes (can be condensation and immersion freezing) to be active. If contributions from deposition mode nucleation can not fully be ruled out I would recommend to change the paper title.

The authors argue that data below 38 K supercooling is excluded from the CNT analysis. From Figure 4 it appears to me that the experiments are affected by homogeneous freezing already at a supercooling around 36 to 37 K (dark red area between 15:45 and 16:00). The droplet diameters given in Figure 2 could be used together with recent literature data for freezing rates of supercooled water to estimate the threshold temperature at which homogeneous droplet freezing starts to affect ice formation in the LACIS experiments. At this point I would like to recommend the LACIS team to conduct, if not yet done so, freezing experiments with supercooled water in order to demonstrate the

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feasibility of the LACIS setup for quantitative ice nucleation rate measurements.

The authors refer to several related papers 'in preparation' which will address issues of coating thickness either directly measured with aerosol mass spectrometers or derived from CCN activation measurements. I strongly suggest to include some experimental information about coating thickness also in the present manuscript.

Specific comments:

First statement of introduction: It is not only the ice containing clouds that affect the climate by light absorption and scattering.

p.15829, l.7: I recommend to avoid the term 'deposition freezing', and suggest instead to distinguish between deposition nucleation (vapour to ice) and freezing modes (supercooled liquid to ice) of ice formation.

p.15829, l.16: Numerous previous studies clearly showed that dust particles act as freezing nuclei in case of droplet activation below -35°C (see e.g. a recent paper by Connolly et al., ACP, 9, 2805, 2009 and references therein).

p.15831, l.3: As stated above, the mobility size as well as type of coating (and probably also coating thickness) are well defined and known in the current experiments, but questions remain concerning the role of unspecified mineral composition, surface roughness and particle morphology.

p.15832, l.5: Why should a 'questionable theory' be applied here? Would recommend to mention which assumptions are questionable and why the authors believe the theory to be appropriate for data evaluation or heterogeneous freezing parameterisation.

p.15832, l.14: . . . density of liquid water molecules . . .

p.15832, l.19: . . . second term represents . . .

p.15833, l.13 to 16: Suggest to give an estimate of the range of these parameters in the given temperature interval, if possible.

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p.15835, l.13: Corona discharges are known to induce radical chemistry. Could this produce impurities to condense on the dust particles and thereby affecting the surface composition?

p.15839, l.8: Replace 'section one' with 'section six' or 'freezing section 1'

p.15840, l.16: Is the seed correction factor of 0.05 also valid for the coated particles?

p.15840, l.21: Is the correction factor C_{MV} caused by a radial particle concentration gradient. Are such gradients the same for aerosol, droplets and ice particles? And if not, did you correct for that effect?

p.15841, l.3: Please specify the CPC and other relevant uncertainties here.

p.15846, l.10: Why can surface area explain the observed increase of parameter 'a'? I thought the diameter and therefore the surface area was kept constant in all experiments.

p.15853, Figure caption: Refer to Equation 8 where the parameters are defined.

p.15853, Figure 4: Any explanation for the the particles in size channels around 100 between 15:30 and 15:45?

p.15865, Figure 12: Are the dashed and dotted curves based on measurements? If so it would be nice to see the nucleation rates instead of ice fractions. If not, the figure should be removed (see also comments above on comparison to other literature data).

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15827, 2009.