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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Investigations of the impact of natural dust aerosol on cold cloud formation" *by* K. A. Koehler et al.

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We would like to thank Dr. Murray for the supportive comments of our work. Below we have addressed each specific comment individually.

Response to Specific Comments (essential selections of original comment above our response):

. . .This is a very interesting paper, in which new and important results are presented and once the comments below have been addressed I recommend it for publication.

We appreciate the positive comments.

1) Title: This title implies that the authors have investigated the impact of ice nucleation

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Interactive Discussion

Discussion Paper

on clouds. Before I read the abstract, I was expecting a modeling study rather than a lab based study. Also, the reference to 'natural dusts' is inaccurate since a number of the experiments have been done with ATD. I suggest something more like: 'Laboratory study of ice nucleation by coated and uncoated mineral dusts' or something similar.

We have changed the title to, "Laboratory investigations of the impact of mineral dust aerosol on cold cloud formation".

2) Abstract ln 15. I think it is actually show that there is a significant difference between ATD and the other dusts between -40oC and -60oC, contrary to what is stated here.

This sentence states that a temperature dependence for the onset of nucleation in the deposition nucleation regime was not observed for any of the samples, although this onset RH is clearly different between the different dusts. We have changed this to say, "Ice nucleated on 1% of dry generated dust particles of a given type at a similar relative humidity with respect to ice irrespective of temperature between -60 and 40oC, however differences in relative humidity for ice nucleation was observed between the different dust types."

3) 19347, ln7-10. In addition, Murray et al. (ACPD, 10, 9695–9729, 2010 recently explored the ice nucleating properties of different mineral types. They showed that kaolinite and montmorillonite have different nucleation characteristics.

Thanks. We have added this recent citation to the references here.

4) 19347, ln 18. Forschungzentrum Karlsruhe has changed its name to Karlsruhe Institute of Technology.

We have corrected this.

5) 19348, ln 21-24. What are the dominant minerals in this size grade of North African dust? A brief discussion on this would be helpful and informative.

We agree and have added the following discussion, "The chemical composition of

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mineral dust is comprised of a variety of clay species that include oxides of silicon, aluminum, calcium, magnesium, iron, potassium, and other salts and metal species. Detailed chemical analysis for a different subset of the SD was reported by Linke et al. (2006)."

6) 19352, ln 4. The word 'hereafter' doesn't make sense here. Revise the sentence.

We changed this sentence to read, "This upper limit is equivalent to what Welti et al. (2009) referred to, and we will refer to hereafter, as the "water breakthrough" RHw."

7) 19353, ln 2-4. Mohler et al (ERL, 2008) also show that the SOA from alpha pinene does not nucleate ice – see their fig 6. This citation backs up the author's argument.

We agree and have added this reference.

8) 19357, ln 17-23. I would not say the results are in 'excellent' agreement. The numbers are not identical and the quoted conditions are not identical. I suggest replacing with 'good'.

We have changed this word as suggested.

9) 19358, ln 5. I do not understand what is meant by 'balance' here. Revise.

By "balance" we meant the rest of the experimental points not discussed before. We have changed this sentence to say, "Connolly et al. (2009) found 1% of their Saharan dust particle distribution freezing at -25°C, more consistent with the majority of our experimental observations."

10) 19359, ln 24, Do the authors mean hydrophilic surface rather than hydrophobic surface?

The word hydrophobic is correct here. The liquid layer is detrimental to ice formation versus a dry hydrophobic surface with exposed ice nucleation sites that would otherwise only be covered by thick liquid layers in the presence of water supersaturations.

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11) 19359, ln 26-29. This sentence needs to be rewritten. It reads that Archuleta did experiments with 10-55 um sized droplets, which is incorrect.

We have revised this to say, “In contrast to the results of Archuleta et al. (2005) who examined coated submicron mineral dust and Zuberi et al., (2002) who examined the freezing behavior of mineral dust inclusions in concentrated ammonium sulfate droplets (10-55 μm), coating. . .”

I also, do not understand what the authors are attempting to say in this paragraph. Please revise. 12) 19359, 1st para. You should also discuss the results of Zobrist et al. (J. Phys. Chem. A 2008, 112, 3965-3975). They observe a significant immersion heterogeneous effect below -40oC.

We have changed the discussion in this paragraph for clarity and to include the results presented by Zobrist et al.:

In contrast to the results of Archuleta et al. (2005) who examined coated submicron mineral dust constituents, Zuberi et al. (2002) who examined the freezing behavior of larger mineral dust inclusions in concentrated ammonium sulfate droplets (10-55 μm), and Zobrist et al. (2008) whose studies included freezing of emulsions with distributions of included ATD, coating by SOA did not lead to a clearly detectable occurrence of heterogeneous freezing by the immersed single ATD particles as the RHw was increased. Heterogeneous freezing was recognized in the studies of Zuberi et al. (2002), Archuleta et al. (2005), and Zobrist et al. (2008) by a clear reduction of the difference of water activity between the freezing conditions and the water activity of the solution in equilibrium with ice, compared to that required for homogeneous nucleation of the pure coating (Koop et al. 2000). For example, Zuberi et al. (2002) found a $\sim$6% reduction in RHw (aw is approximately equal to RHw for particles greater than 200 nm) for freezing compared to the homogeneous nucleation of pure ammonium sulfate particles. In the present study, there was no significant difference in the freezing conditions of the SOA coated ATD particles as compared to pure ammonium sulfate drops of similar size (the

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homogeneous freezing conditions of the pure SOA is unclear). This suggests that the heterogeneous freezing process for concentrated solution droplets below -40°C may depend on the chemical species coating the dust material, the thickness of the coating, and the amount and size of dust material contained within the drop. . It is possible that large droplet and emulsion experiments emphasize the impact of larger or multiple aerosol particles in contrast to single particle studies, but this topic will require further research. Again, interestingly, inhibition of freezing nucleation was not apparent in the mixed-phase regime above water saturation in the present studies.

13) Discussion on 19362. Can the authors comment on why the SOA should deactivate ice nuclei in the deposition mode, but not in the condensation/immersion mode? Zobrist et al and also Zuberi show that when the 'coating material' is soluble and in an aqueous state heterogeneous nucleation is still active. Eastwood et al. (GEOPHYSICAL RESEARCH LETTERS, VOL. 36, L02811, doi:10.1029/2008GL035997, 2009) show that when kaolinite is immersed in sulphuric acid and ammonium sulphate droplets it nucleates at a much higher RH than when uncoated, but is still active (i.e. nucleates below homogeneous). This seems relevant and should be discussed.

This is certainly an interesting question, and one which we cannot fully answer at this point. It is likely, as discussed above that, "the heterogeneous freezing process for concentrated solution droplets below -40°C may depend on the chemical species coating the dust material, the thickness of the coating, and the amount and size of dust material contained within the drop. It is possible that large droplet and emulsion experiments emphasize the impact of larger or multiple aerosol particles in contrast to single particle studies, but this topic will require further research." We feel this is a topic for future research and so to say any more is not merited at this time.

14) The difference between Koehler et al.'s data and the previous work is that the coatings in the previous studies were soluble. SOA may have a low solubility and may physically block the access of water vapour to the dust particles rather than binding to active sites etc. However, if this is the case it is unclear why nucleation above -36oC

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remains active in the presence of SOA. One thought is that maybe the SOA solidifies or becomes very viscous or sticky at lower temperatures or maybe becomes insoluble at lower temperatures. This discussion doesn't necessarily need to be included in the revised version, but I mention it because I'm interested!

Certainly this is a very interesting topic and one that is being considered by our group and others, but perhaps is best left for future research.

15) One thing that is not discussed and should be is why at around the threshold for homogeneous nucleation of pure water droplets the characteristics of ice nucleation apparently shift. Above about -36oC it is always immersion or condensation freezing(the liquid state is involved), but below -40oC it is clear deposition nucleation on the 'clean' dusts. Is the match with the homogeneous freezing temperature of water just a coincidence or is there some physical basis for this?

This is an issue that has puzzled us as well. We do not feel there is compelling evidence for a physical basis from our data or a review of the literature at this point. It has been noted by others (e.g., Field et al. (2006)). Certainly this is an issue that should be explored further in the future. We have added this issue in the first paragraph of section 3.5, "It is interesting that the observed shift from deposition nucleation to heterogeneous freezing occurs at approximately -36°C, similar to the temperature at which homogeneous freezing occurs. It is unclear if there is a physical basis for this or if it is simply a coincidence. "

16) P19364, ln 27. I disagree, based on fig 6 the activation is not complete. In the homogeneous case it is only getting to 20%, and in the heterogeneous case it is getting to about 50%. Why is it not complete?

We have removed the "complete activation" description as it was not appropriate. Other similar homogeneous freezing curves are shown in the noted publications, where known reasons for the overturn of the steep curve at high fractions nucleating are discussed and other reasons are speculated on. The higher fraction of dust particles

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freezing is achieved prior to water saturation and is not likely achieved via a condensation freezing process, so was not meant to be the emphasis of the figure. Instead, the emphasis is on the broader character of ice activation at lower RHw. The discussion now reads, "Figure 6 shows activation curves for dry generated CID versus 200 nm ammonium sulfate particles that freeze homogeneously at -40°C in the CFDC. Each point is an average over ten seconds of data. The solid line is the homogeneous freezing representation for perfectly monodisperse ammonium sulfate as predicted from Koop et al. (2000). It is clear that the experimentally-observed activation by homogeneous freezing is a very steep function of RHw, and is well represented by the water activity based parameterization excepting the need to consider non-monodispersity of the aerosol and some unresolved CFDC factors that can limit the maximum fractions of hygroscopic particles activating by homogeneous freezing (DeMott et al., 2009a; Richardson et al., 2010). In contrast, activation of the dry-generated CID (and other dust samples) occurs over a broad span of 10-20% RHw."

17) I like the discussion on the importance of not assuming a single threshold nucleation RH for all IN in models. I fully agree with this. In fact, nucleation on glassy aerosol also occurs over a wide range of RH conditions (Murray et al. Nat. Geosc. 2010).

Indeed this is an important issue.

18) P19365, ln 24. SOA is referred to as being hygroscopic. Is this material really hygroscopic? I think of sulphuric acid or NaCl as hygroscopic, but I would imagine most of the components of SOA generated from alpha pinene are relatively insoluble and therefore non-hygroscopic.

Yes, we agree and have changed this to simply say "coating" because as is discussed in the previous sections it is unclear how the different types of coatings affect ice nucleation properties of dust.

19) P19366 ln 27. Eastwood (2009, see above) and Dymarska (JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 111, D04204, doi:10.1029/2005JD006627, 2006) both

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show that larger kaolinite particles (supermicron) can nucleate ice at lower RH.

While these studies do show similar results, for brevity of the discussion here and in the rest of the manuscript, we have limited ourselves to discussion of studies that use mineral dust samples, not pure clay species.

20) P19367, ln 3. (also in other places). Mineral dust particles are referred to as 'freezing'. Mineral dust particles can nucleate ice and cause liquid to freeze. Please correct.

We have changed this sentence to read, "Larger particles contained within the polydisperse aerosol streams were observed to freeze at a level representing 1% of all particles at temperatures as warm as -20°C, a trend which appears to continue to warmer temperatures for larger dust particles (Salam et al., 2006; Kanji and Abbatt, 2006; Knopf and Koop, 2006) and for lower frozen fractions (DeMott et al., 2010)."

Specific editorial comments: 1) 19346, ln 4. The word 'ability' is in the wrong place in the sentence. Revise. We believe this is correct as it is.

2)19347, ln 1. Delete 'grown'. This has been deleted.

3) 19360, ln 5. Delete extra 'an'. We do not see an extra word here.

4) P19366, ln 19. Insert a new paragraph after 'DeMott et al. (2010).' The paragraph break has been added.

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