Atmos. Chem. Phys. Discuss., 13, C3084–C3092, 2013
www.atmos-chem-phys-discuss.net/13/C3084/2013/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Laboratory studies of immersion and deposition mode ice nucleation of ozone aged mineral dust particles" *by* Z. A. Kanji et al.

Anonymous Referee #1

Received and published: 5 June 2013

Kanji et al. report the measured ice nucleation properties of two types of mineral dust, in both the deposition and immersion regimes, and the effect of high levels of ozone exposure in a tank reactor on the ice nucleation properties. There is only one previous report that studied the effect of ozone on ice nucleation by mineral dust, so this study is worthwhile. Though it needs to be pointed out that as ozone is a secondary pollutant formed by photochemical reactions of other pollutants, that it is unlikely that dust particles would be exposed only to appreciable levels of ozone during atmospheric transport and not also be exposed to other pollutants. The authors used appropriate methods to determine the results, and present a detailed analysis of their results. Unfortunately, the data analysis performed is often quite lacking, and the results are very over interpreted. It is hard to distinguish a significant difference between the ice nucleation properties of many of the systems, and thus many of the rather strong claims made by the authors are not in fact supported by the data. The mechanistic interpretation of the observations is also not justified in many cases. Given these serious deficiencies, this manuscript requires major revisions before it might be acceptable for publication in ACP. I think the data measured in these experiments is of high quality and is valuable, but its value is hampered by the manner in which the data is currently analyzed and interpreted.

The most critical issue is in how similar the ice nucleation response appears to be from different systems. For example, Kaolinite (Ka) and Ka with low-exposure ozone overlap each other in Figs. 7A and somewhat in Figs. 8A and 10A. All the 3 ATD systems overlap extensively in Fig. 7B, 8B, and ATD and LE-ATD overlap extensively in Figs 9B and 10B. Yet when the authors describe these different systems they present the data as if there are real and significant differences between them. I.e. that ozone (and different levels of ozone) have clear effects on the ice nucleation properties. This is just not supported by the data they present in many cases. The discussion of the results requires major revision to present the data in a more honest manner. It would also help if error bars were provided for all three datasets in Figs. 7A&B.

The plots of ice active fraction at 95% RH versus temperature (or for immersion freezing) are the most meaningful ways to plot the results that require the fewest assumptions to be made (Figs. 8 and 9). So I would base the assessment of the effect of ozone primarily on these figures (as well as full RHw scans, as I discuss below). For ATD there is a pretty clear loss of ice nucleation ability from ozone exposure in the deposition regime, but this is one order of magnitude loss at most. In the immersion regime the effect is only clear with high O3 exposure. For Kaolinite, there may be an enhancement of deposition ice nucleation ability with lower O3 exposure, but the data is quite scattered so this effect is not clear. The loss of IN ability at higher O3 exposure is more clear. In the immersion mode the loss of ice nucleation ability after Ka was exposed to O3 is pretty clear. Why low exposure would increase IN ability of Ka in the deposition mode but decrease it in the immersion mode is a mystery. Based on the data presented, I really do not think the authors can conclude much more from their data. They should be very careful to not over-interpret or over-sell their results. The effects of ozone are just not clear enough in many cases to support many of the conclusions the authors state. Even the largest observed effects on IN ability are limited to one order of magnitude change at most – these are not hugely significant changes, though the authors state that they are.

When discussing results from other groups, it is very important to keep in mind the temperature range and ice nucleation regime the measurements were made at. For example, for the ambient measurements of aged/coated particles in Mexico City and Los Angeles, these measurements were made at cold cirrus temperatures of 233-205 K. The effects of aging/coatings might be very different at cirrus temperatures compared to mixed-phase cloud temperatures, as are studied here. (Page 8707, line 5)

The stated discrepancy between the effects of coatings on ice nucleation from laboratory versus field measurements is also inaccurate. The recent understanding seems to be that coatings impair deposition ice nucleation, but may not impair immersion freezing. It is critical to distinguish between these two modes when discussing any effect of aging/coating on ice nucleation. It is also important to state in what mode the ice nucleation measurements were made. (page 8707, line 15)

The paper is rather long and wordy, considering the amount of data that is actually presented. This makes the paper difficult to follow. The authors do present a detailed summary of related work throughout the paper, which is appreciated, but they may want to trim this as it does add a lot of length.

Abstract, lines 19-22: An enhancement is discussed in one sentence, and then immediately after a suppression of IN ability. This is confusing.

Section 2. The experimental overview/summary is not necessary.

Section 3. The summary at the beginning is also not necessary.

Section 3.1. It would help if the motivation behind deriving the ozone update kinetics was stated upfront.

3.1. No references are given to the composition of ATD.

Ozone uptake on mineral dust typically exhibits a fast initial decal, and then a slower constant decay, as observed here. How were the initial (fast) uptake kinetics determined? And why were the initial kinetics used here, when the dust is exposed to ozone for 2 hours? The slower kinetics that persist seem more relevant to this work.

Ozone decay kinetics on dust are inversely related to the concentration of ozone used. The authors state this, yet seem to ignore this important fact by linearly extrapolating from their ozone exposures to other conditions to compare with those results, or to extrapolate from their high O3 concentrations to atmospheric conditions. This is not justified, the kinetics are not first order with [O3]!

I do no see how dust will be exposed to significant levels of ozone and no other pollutants that might age/coat the surface. NOx is required for ozone production, as the authors discuss (page 8719, line 23). In fact, the de Reus et al. (2000) study cited here concluded that half of the ozone loss observed was due to direct uptake of ozone on dust, while the other half was an indirect loss caused by the uptake of nitrogen oxides to the dust. There is no way for dust to be exposed only to ozone and to no other pollutants in the troposphere. The surface sites can also regenerate after reacting with ozone, this is what allows mineral dust surfaces to catalytically destroy ozone.

The Fine mode (A2?) of Arizona Test Dust was used here. The authors should be aware that many other reports have used the Ultrafine (A1) fraction of ATD for ice nucleation work. These fractions have different particle size, and are also processed differently. I believe A2 is washed while A1 is not.

More details regarding how the dust size distribution (did not) changed over the several hours of the experiment should be described. If the size distribution was changing this could greatly affect the IN activity. The particle concentrations did decrease substantially during the experiment.

Merging SMPS and APS size distributions is not straight-forward, since two different diameters are being measured (mobility and aerodynamic), and only one depends on particle density. There are published methods for doing this merging that the authors should implement. The authors should also be cautious in relying solely on the mode diameter to describe the polydisperse size distribution.

I assume that the relative humidity of the IN chamber was scanned at a fixed temperature, though this is not discussed. How were these scans performed? At what scan rate? It is very important that the full scans be shown.

No discussion of the quantification of the instrument's background IN counts is presented. This is a critical issue for all CFDC-like instruments. The IN background must be measured regularly by filtering the sample air. How was this done, and what were the typical background IN concentrations? A properly performing CFDC should have background IN of just a few per L. Along with this the authors should discuss if any large dust particles caused a false IN signal in the OPC or IODE detectors. This can easily be determined by operating the ice chamber at room temperature, for example. There was supermicron dust present in their samples, and the impactor may not effectively remove all supermicron particles.

The restriction of the IMCA instrument to measuring immersion freezing only for IN fractions > 0.1 is quite concerning. This is a high level of IN activity, only exhibited by large particles from very active mineral dust samples and at low temperatures. Size selected submicron dust rarely exhibits such high activity. Important immersion freezing that occurs below this high threshold will be missed. This must be discussed.

While it is commonly used, reporting conditions for ice nucleation at some arbitrarily chosen activated fraction is not a useful way to analyze ice nucleation experiments. This reduces the complexity of the ice nucleation behavior over a range of T and RHw to just one number, at some arbitrary condition. In fact even the same research group cannot agree on what activated fraction to use. 0.1% is used here, but this group has previously used 1%. What is the justification for the choice of AF used here? The best justification would be in full scans of the IN fraction versus RHw at fixed T were shown. Then the full ice nucleation response will be revealed. It is much more meaningful to instead report the IN fraction observed at a chosen RHw that represents an ice nucleation mode, such as was done using RHw = 95%. This is a much more meaningful analysis.

The other important problem with using AF to analyze the data is that depending on the activity of the dust, the AF will cause you to report the ice nucleation response in different modes. An active dust will have AF = 0.1% in the deposition regime, while a less active dust will not achieve the same AF until the immersion mode is reached. As we know that the ice nucleation properties of dust particles respond differently to aging in the different modes, one must be careful that they are comparing measurements from the same modes. The authors should focus their analysis on the measurements at 95% RHw for the deposition mode (Fig. 8), and the immersion mode data using IMCA. Activated fraction is poorly constrained and not meaningful. Again, some exemplary full RHw scans should be presented. The authors appear to realize this important issue, yet continue to analyze the data in this confusing manner: "The representation of data in Fig. 8 and the observations made thereof are an indication that the cross section of data at AF = 0.1 % (as presented in Fig. 7) can be limiting and not fully representative of the ice activation spectra obtained for deposition mode nucleation, especially given the onset RHw for both LE-ATD and ATD data were mostly within the instrument uncertainty in Fig. 7." (Page 8724, line 15)

In many instances the authors could be more clear what they are referring to. For example, they state that another paper agrees with their conclusions, yet do not state their conclusions (Page 8724, line 1). Or they state that other data agrees with their observations, but do not state their actual numbers to facilitate this comparison (page 8725, line 9).

Section 3.3. The immersion freezing properties of the dust without ozone exposure should be discussed first, and compared to other published results, before the effect of ozone is discussed. This section jumps around a lot and is hard to follow.

Page 8725, line 23: “The immersion freezing of 300 nm ATD particles has been reported by Niedermeier at al. (2010), however T50 % occurred at T < 236 K in the homogeneous freezing regime, suggesting that the particles did not freeze heterogeneously in contrast to the current work.” This faulty analysis is based on the notion that only if particles have an extremely high ice active fraction of 50% are they considered to freeze heterogeneously. This is completely incorrect, and is a good example of the problems with the IODE’s very high detection limit of AF > 0.1. Niedermeier et al. did observe 300 nm ATD particles to be good immersion freezing nuclei, just not at the very high AF required by these authors.

Page 8726: These are all still very high levels of immersion freezing activity, yet the authors discuss the data as if a decrease in AF of 33% is a hugely significant change. A very large fraction of the dust can still nucleate ice even after ozone exposure. Again, the effect of ozone is overstated here.

Section 4.2. The brief discussion of stochastic versus deterministic models of heterogeneous ice nucleation was nicely done and appropriate. The authors might also cite the recent sensitivity analysis of (Ervens & Feingold, 2013) that concluded that ice nucleation is least sensitive to time compared to temperature, particle size, and contact angle.

n_s(t) needs to be better explained to be clear to the readers. What does it describe?

Page 8733, line 3: “ATD responded differently to the O3 exposure in both deposition and immersion mode, i.e. no significant enhancement in ice formation was observed. This is not surprising however given that the BET surface area of ATD is 50 % that of Ka and thus presents a smaller surface area that can be altered due to heterogeneous oxidation of O3.” Wouldn’t the smaller BET surface area suggest a smaller effect of O3 on ATD versus Ka, as opposed to no effect that the authors suggest here? This interpretation does not seem justified.

Page 8733: Surface oxides do not only form by reaction with aluminum minerals. The observed different response for ATD vs. Ka is not at all well explained here by referring to their different compositions. I do not think the authors can really say much about what is actually happening at the mineral surface of the two systems when ozone reacts with it. Also, given the long exposure times and high [O3] used here, I think all the surface sites will be saturated by O2 or other oxygen species, for both dust systems. This is supported by the fact that the ozone kinetics were observed to be in the slow and constant regime for most of the 2 hours of exposure, following the short rapid loss period.

Page 8734: “For immersion freezing HE-ATD showed a larger suppression in ns than HE-Ka. A reason could be due blocked reactive sites on the surface if ATD that are likely ice nucleation active sites arsing[sic] from the physisorption of O3 that occurs on silica. . .” In the preceding paragraph you stated that less surface oxides would form on ATD due to the lower Al content, and that surface-bound O2 would be released from ATD, regenerating the surface sites. That contradicts what you have proposed here. None of this is adding up.

Section 4.5. I do not see how the conditions used here (high [O3] for 2 hours) are “atmospherically relevant conditions”. The authors also seem to focus on comparing their work to the others that have shown an enhancement or impairment of IN ability due to aging. It would be more appropriate to discuss all effects that have been observed from aging. Many studies have show that aging does not impair immersion freezing. Again, it is important to distinguish the effects on deposition vs. immersion ice nucleation.

Page 8736, line 1: Montmorillonite is an aluminosilicate clay, and much more similar to Ka than ATD. This comparison doesn't make sense.

Page 8712, line 24: "The IN counters have been extensively described in previous work." These works should be cited.

Page 8716, line 24: What is IASSD? There is an overuse of acronyms in this paper, and it becomes confusing.

Page 9738, line 2: Is "50-0.1 particles cm-3" a typo?

I don't think Figures 1-3 are necessary. Figs. 2 & 3 are available in other papers that describe these methods.

Table 2. Uncertainty ranges should be given for individual values.

Table 5. A Lot of significant figures are used here.

Figure 11. The agreement of this data with the fit from Niemand et al. looks quite poor to me. While their fit does go through the center of your data, the slope is very different. The text presents this as good agreement – this is not justified. It is interesting that all the fits converge at low T for the ATD but not for Ka. Discuss this?

Ervens, B., & Feingold, G. (2013). Sensitivities of immersion freezing: Reconciling classical nucleation theory and deterministic expressions. Geophysical Research Letters. doi:10.1002/grl.50580

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 8701, 2013.