**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Ice nucleation from aqueous NaCl droplets with and without marine diatoms" *by* P. A. Alpert et al.

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The authors would like to thank the referee for reviewing our manuscript. Below we give a point by point respond to the issues raised by the referee.

This manuscript investigates (1) homogeneous nucleation of NaCl droplets and (2) heterogeneous nucleation of NaCl droplets containing marine diatoms. The measurements appear to be carefully performed, and the results are quantitative in nature. Because of this they are useful for assessing the importance of marine diatoms in ice cloud formation. However, I have several comments regarding the interpretation of the data that need to be addressed before publication in ACP.

We thank the referee for this kind comment.

Page 8302, line 20: "It should be noted that if the homogeneous freezing curve parameterization suggested by Koop et al. (2000b) were used in place of the one suggested by Koop and Zobrist (2009), then a significantly better agreement of our ice nucleation data with predictions at lower water activity, a_w, would be achieved." This statement suggests that only the parameterization by Koop and Zobrist (2009) was used in Figure 1 to predict homogeneous freezing. However, the caption for Figure 1 suggests that the homogeneous freezing parameterization is based on Koop et al. (2000b) AND Koop and Zobrist (2009). I am confused by these two conflicting statements. Some explanation is required here.

We apologize for the confusion here. We simply meant to acknowledge that Koop et al. (2000) first parameterized homogeneous freezing according to the a_w based homogeneous ice nucleation theory, but that later Koop and Zobrist (2009) altered this parameterization due to updated water vapour pressures over supercooled liquid water and ice given the results of work by Murphy and Koop (2005). The homogeneous freezing curve shown in Fig. 1 is a shift of the melting curve, in which we use the parameterization provided by Koop and Zobrist (2009). To make this point clearer we omit the sentence "It should be noted that if the homogeneous freezing curve parameterization suggested by Koop et al. (2000b) were used in place of the one suggested by Koop and Zobrist (2009), then a significantly better agreement of our ice nucleation data with predictions at lower a_w would be achieved." We also have changed the figure caption of Fig. 1 from "The solid line represents the predicted homogeneous freezing curve (Koop et al., 2000b; Koop and Zobrist, 2009)." To "The solid line represents the predicted homogeneous freezing curve (Koop and Zobrist, 2009)." We also correct this issue in the figure caption for Fig. 4.

Page 8304, line 23: "Deviations of observed ice nucleation distributions from the fits were mostly found at higher temperatures due to possible heterogeneous freezing events." There are also significant deviations from the fits at low temperatures for some of the measurements. Can the authors suggest an explanation for these deviations?

Significant deviations of observed ice nucleation distributions from the fits for lower temperatures occur for aqueous NaCl droplets with lowest a_w of $0.806 - 0.851$. At these lower a_w values, uncertainties in a_w can have a greater effect on droplet composition and therefore on freezing temperature. Thus, these deviations likely reflect our experimental uncertainty in a_w. We add on page 8303, line 26: "Deviations of observed ice nucleation distributions from the fits for lower temperatures occur for aqueous NaCl droplets with lowest a_w of $0.806 - 0.851$. This is likely due to our experimental uncertainty a_w."

Page 8306, line 3: "however, this effect is not critical for deriving Jhom as a function of T due to the goodness of the fit in Fig. 2 and the insignificant number of heterogeneous compared to homogeneous freezing events as previously discussed." I don't think the fits in Fig. 2 show that heterogeneous freezing will not impact the calculations of Jhom. Figure 2 is a fit to the entire data set; whereas, Jhom was calculated for small temperature intervals. In a small temperature interval a few heterogeneous nucleation events can drastically change the calculation of Jhom. I think a better procedure would be to exclude the first 15% of the freezing events when calculating Jhom.

The purpose of Fig. 2 is to show that the great majority of droplets freeze homogeneously. As stated on page 8303, line 26, even when only accounting for freezing data within the 10th and 90th percentiles, the freezing distribution and their agreement with the fits, do not change significantly. Thus, heterogeneous freezing events that occur at warmer temperatures reflect a minority of freezing points. Also, omitting any percentage of observations at warmest temperatures would not change J_{hom} reported in Fig. 3. This is because at a specific T, nucleation events that have occurred at warmer T do not contribute to J_{hom} (see Eq. 3). J_{hom} values for a given a_w which extend to higher temperatures and do not show a strong increase with decreasing temperature, are most likely affected by heterogeneous freezing events. As previously stated, heterogeneous freezing constitute the great minority of events and do not contribute to a significant increase in the slope of J_{hom}. For these reasons we respectfully disagree that we

should arbitrarily exclude the first 15% of the freezing events when calculating J_{hom}. We will, however, add the following sentence to page 8305, line 6: "J_{hom} values for given a_w which extend to higher temperatures and do not show a strong increase with decreasing temperature, are most likely affected by heterogeneous freezing events. For example, the freezing data for aqueous NaCl droplets with $a_w = 0.900$ in Fig. 3 does not show a strong increase in J_{hom} for temperatures between $220 - 226$ K, and remain almost constant at values below 10^5 cm^{-3} s^{-1}. However, J_{hom} values increase significantly from 220 K to 214 K as the homogeneous freezing limit is approached." We hope that the reviewer finds this explanation and change satisfactory.

Page 8305, line 9: "Within the theoretical uncertainty, JKoophom agrees with the experimental data." I do not come to this conclusion when looking at Figure 3. For example at a aw of 0.806 the measured J values can vary from the theory by more than 5 orders of magnitude for some temperatures! Also the slopes of the measured J values are very different from the slopes of the theoretical J values at lower water activities.

There is only one instance where predictions of J_{hom} following Koop et al. (2000) are not in agreement with our observations employing an uncertainty in a_w of ± 0.025. This occurs for $a_w = 0.806$. It should be noted that at $a_w = 0.800$, Koop (2004) gives an uncertainty of ± 0.05 resulting in ± 12 orders of magnitude in uncertainty of J_{hom} (see Fig. 9 of Koop (2004)). We did not include two different uncertainty ranges for different a_w regimes, not wanting to further complicate the data analysis. Since we state (see previous response) that freezing events at higher temperatures for fixed a_w are likely due to heterogeneous ice nucleation, overall there is agreement between our data and predictions. To further clarify this issue we add the following sentence at page 8305, line 10: "A potential exception are J_{hom} values obtained for $a_w = 0.806$ for which J_{hom}^{Koop} under predicts our observations. This may be due to the occurrence of heterogeneous ice nucleation events and/or the unknown behavior of supercooled aqueous NaCl solutions, especially at this low a_w value. It should be noted that the uncertainty of the a_w based homogeneous ice nucleation theory for $a_w = 0.800$, is given

as ± 0.05 in a_w which translates to ± 12 orders of magnitude uncertainty in predictions of J_hom (Koop, 2004)."

Abstract: the authors suggest that homogeneous nucleation rate coefficients were in agreement with water activity theory. Similar to the above point, this statement should also be modified to reflect the differences in Figure 3.

As discussed in previous response, when accounting for the experimental uncertainty of homogeneously frozen droplets and the uncertainties of the a_w based homogeneous ice nucleation theory, predictions and experimental data are in agreement. For this reason we do not feel that this statement needs to be changed.

Page 8309, line 15: "According to classical nucleation theory, omegahet and Jhet reflects an exponential dependence on temperature (Pruppacher and Klett, 1997) suggesting that heterogeneous ice nucleation due to intact and fragmented diatoms follows a time-dependent freezing process, in line with classical nucleation theory." I do not thing that this conclusion is well supported by the data. For example, the data could follow a time independent process and still have an exponential dependence on temperature.

We do not state in this manuscript that heterogeneous ice nucleation follows a time dependent or time independent description. We present the analyses of our data applying both approaches for interpretation. According to classical nucleation theory, J_het varies exponentially with temperature. This is reflected in Fig. 8a and 8b of our manuscript. Therefore we suggest that heterogeneous ice nucleation may follow a time-dependent freezing process. However, we have also interpreted our heterogeneous ice nucleation data applying a time-independent freezing process. These results are plotted in Fig. 8c which also indicates that the differential ice nuclei spectra, k, and cumulative ice nuclei spectra, K, vary exponentially with temperature. This is clearly stated on page 8310, line 21 until page 8311, line 2. Since the singular approach has currently no theoretical foundation, the expected temperature dependency of $k(T)$ and $K(T)$ is not known.

C2877

Since k, K, and J_het are based on fundamentally different physical principles (if known) and are expressed in different units, a similar temperature dependency may not show the ambiguity of the data with respect to either nucleation description. Thus, a final statement of the underlying nucleation process cannot be given and for this reason we present both analytical descriptions.

Abstract: "Our results confirm, as predicted by classical nucleation theory, that a stochastic interpretation can be used to describe this nucleation process." Similar to the above comment, I think this statement is too strong and not supported since the data doesn't differentiate between the stochastic or the singular model.

We apologize for the confusion with this statement. This sentence is in regard to homogeneous, and not heterogeneous, ice nucleation. In response to the referee comments, will add the words "homogeneous ice nucleation", to avoid confusion. On page 8292, line 14, the sentence now reads, "Our results confirm, as predicted by classical nucleation theory, that a stochastic interpretation can be used to describe the homogeneous ice nucleation process."

Page 8312, line 7: "Assuming typical sea salt concentrations of 80 cm-3 with mean dry diameter of 200nm (O'Dowd et al., 1997) and a wet diameter of 480nm at 90% RH (Zhang et al., 2005; Lewis and Schwartz, 2006), and applying Jhom = 106 cm-3 s-1 at a temperature of 215 K (Fig. 3), Phom could reach 0.3 ice particles L-1 (air) min-1." The authors are using sea salt concentrations measured in the boundary layer and applying these numbers to cirrus cloud conditions in the free troposphere, I think. Is there any evidence that these number densities of sea salt particles measured in the boundary layer are applicable to the free troposphere and cirrus conditions? If not, the authors should weaken their conclusions significantly.

The main purpose this paragraph is to provide an example for calculating the ice particle production rates, $P_\mathrm{hom}^\mathrm{ice}$ from experimental derivations of the homogeneous ice nucleation rate coefficient, J_hom.

C2878

Previous studies have identified and quantified sea salt particles in the free troposphere (Cziczo et al., 2004; Ikegami et al., 1994, 2004; Brock et al., 2011; Hara et al., 2006). A study by Cziczo et al. (2004) found that sea salt particles were present at about 12 km of altitude employing the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument, and that when ice was present, sea salt was preferentially included in ice crystal residues. Ikegami et al. (1994) and Ikegami et al. (2004) observed that at an altitude of 12 km, over half of a total aerosol particle concentration ranging between $0.05 - 100$ cm^{-3} for particle diameters between $0.15 - 0.5$ μm, were sea salt. In a recent study, Brock et al. (2011) measured submicron aerosol particle concentrations of 371^{+311}_{-169} particles cm^{-3} (STP) of air up to 7.4 km, and reported that sea salt particles constituted 4% and 23% of particles with diameters between $0.15 - 0.7$ μm (fine particles) and $0.7 - 3$ μm (coarse particles), respectively. This amounts to sea salt particle concentrations as much as 27 cm^{-3} and as little as 8 cm^{-3}. We do acknowledge that sea salt particles are not always observed in sufficient quantities (Hara et al., 2006) to make a significant difference to ice nucleation processes, given that aerosol particle composition is highly variable and depends on atmospheric dynamical conditions and physical and chemical processing.

In response to the referee's suggestion, we will remove the word "typical" and modify our calculation employing a particle concentration of 10 cm^{-3} to the sentence starting on page 8312, line 7 to read the following, "We assume sea salt concentrations, estimated here from field observations of aerosol particle concentrations in the free troposphere as 10 cm^{-3} (Cziczo et al, 2004; Ikegami et al., 1994; Ikegami et al., 2004; Brock et al., 2011; Hara et al., 2006), with mean dry diameter of 200 nm and a wet diameter of 480 nm at 90% RH (Zhang et al., 2005; Lewis and Schwartz, 2006), and applying $J_{\mathrm{hom}} = 10^6$ cm^{-3} s^{-1} at a temperature of 215 K (Fig. 3), $P^{\mathrm{ice}}_{\mathrm{hom}}$ could reach 0.035 ice particles L^{-1} (air) min^{-1}." The sentence starting on page 8312, line 13 will now read the following, "Thus, after 30 min at these atmospheric conditions, approximately 1 ice crystal per liter of air could form."

C2879

Page 8315, line 17: "At T = 220 K and RH = 85% (Haag et al., 2003; Strom et al., 2003) applying the same diatom concentration for cirrus cloud formation assuming ice nucleation does not depend on surface area, we derive omegahet = 0.51 s-1 and Phet = 3.5 ice particles L-1 (air) min-1." These numbers seem to be misleading. For example after 10 minutes the number of ice particles would be 35 L-1 due to diatoms, but the number density of diatoms used in these calculations was 0.1 L-1, unless I misunderstood the calculations. In this case the number of ice particles is 350 times larger than the number of ice nuclei. This comparison suggests that there is a problem in the method used by the author to extrapolate their laboratory data to the atmosphere. If the number of ice nuclei are 0.1 L-1 then I would expect that the maximum number of ice particles would be 0.1 L-1 assuming no multiplication mechanism. Perhaps I am missing the authors point. In this case the authors should clarify their point.

The referee is commenting on the calculation of the ice particle production rate, $P^{\mathrm{ice}}_{\mathrm{het}}$, in units L^{-1} min^{-1} (air) employing the ice nucleation rate, ω_{het}. This ice particle production rate depends on the available numbers or surface areas of IN. It gives the efficiency of, or how rapid, a given population of IN will form ice crystals. This should not be mistaken by the actual ice crystal concentration which depends on the overall availability of IN as pointed out by the referee. $P^{\mathrm{ice}}_{\mathrm{het}}$ quantifies the evolution of ice particle production and, in other words, how fast or slow ice is produced. To make this point clearer we add the following sentence to page 8314, line 24 and page 8315, line 20: "This indicates that all available diatoms would nucleate ice within seconds."

While recalculating $P^{\mathrm{ice}}_{\mathrm{het}}$ values, we found mistakes in derivations of $P^{\mathrm{ice}}_{\mathrm{het}}$ from particle numbers, ω_{het}, J_{het}, and K. We have recalculated our values of $P^{\mathrm{ice}}_{\mathrm{het}}$. The changes are as follows. Beginning in the middle of page 8314, line 26: "the corresponding $P^{\mathrm{ice}}_{\mathrm{het}}$ is equal to 0.001 L^{-1} min^{-1} (air) and 0.0001 L^{-1} min^{-1} (air), respectively." In the middle of page 8315, line 19: "$P^{\mathrm{ice}}_{\mathrm{het}} = 3.06$ ice particles L^{-1} min^{-1} (air)." In the middle of page 8315, line 22: "$P^{\mathrm{ice}}_{\mathrm{het}} = 0.022$ L^{-1} min^{-1} (air) and $P^{\mathrm{ice}}_{\mathrm{het}} = 0.0022$ L^{-1} (air), respectively."

The changes in $P^{\mathrm{ice}}_{\mathrm{het}}$ do not affect subsequent discussions except in one place: We

C2880

have altered our discussion by removing the following sentence beginning on page 8315, line 1: "From this estimate, when employing $K(T)$ however, we find that only a small fraction of diatom fragments would have ice active sites under these specific conditions, resulting in much lower ice crystal concentrations than for estimates employing a time-dependent analysis."

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C2881

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