Heterogeneous ice nucleation ability of aerosol particles generated from Arctic sea surface microlayer and surface seawater samples at cirrus temperatures

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Summary

The authors present new data on the ice nucleation ability of aerosol generated from Arctic seawater samples. Further experiments investigated the ice nucleation ability of aerosols comprised of inorganic sea salt and aerosols generated from a culture of the diatom *Skeletonema marinoi*. Using active site densities, conditions at the onset of nucleation, and median freezing temperatures, the team quantified ice nucleation in both the mixed-phase cloud regime (~248-268 K) using off-line droplet freezing techniques and in the cirrus cloud regime (~210–235 K) using the AIDA chamber. The ice nucleation abilities of particles was compared between the mixed-phase cloud and cirrus cloud regime.

General Comments

The data presented here make a notable contribution to the field of aerosol-cloud interactions by systematically investigating the ice nucleation abilities of sea-spray analogues at cirrus-relevant conditions. Although INPs derived from Arctic seawater have been the topic of several recent publications, few have studied the ice nucleation abilities at temperatures cold enough to speak to their potential impact on cirrus cloud properties. Although ice nucleation in the cirrus regime is less frequently studied than in the mixed-phase cloud regime, the climatic impact of cirrus clouds means aerosol-cloud interactions at cirrus temperatures warrant further exploration in studies such as this one.

The authors should be commended for investigating a relationship between the ice nucleation abilities of seawater-derived particles in the mixed-phase and cirrus cloud regimes. This is an interesting addition that I hope future studies will expand on. The authors should also be commended for their efforts to compare their results to previous studies and discuss possible scientific and methodological reasons for differences.

I therefore support the publication of this manuscript in ACP pending minor revisions. Below, I outline some requested revisions, while also providing a few questions and comments to clarify some of the text's conclusions.

Primary Comments

1. A note on ice nucleation terminology — I encourage the authors to consider whether "immersion freezing" is truly the best term to describe the process of ice nucleation upon deliquescence (or in pre-deliquescence hygroscopic growth) but below liquid water saturation in the cirrus cloud regime.
    a. Although I acknowledge that other publications have referred to this process as "immersion freezing" — and I do not insist that an alternative term be adopted here — it is somewhat unintuitive to refer to freezing processes below water saturation as immersion freezing. The authors themselves allude to my concerns in line 101: "Note, immersion freezing in this case is different to immersion freezing under mixed-phase cloud conditions since it occurs below liquid water saturation."
    b. As a possible alternative, I might suggest the term deliquescence-freezing, as proposed by Khvorostyanov et al., 2004.

2. The authors present data seeming to indicate that at cold temperatures (<217 K), the fractional ice activation of inorganic sea salt increases after reaching the full deliquescence relative humidity. (I refer to the data in Figure 6a.)
    a. This is counterintuitive to me, as I would expect full deliquescence of inorganic salt particles to result in a totally aqueous solution that would preclude further particles from heterogeneously nucleating ice. Can the authors please clarify or explain this in the text?

3. The differences between the present study's findings and those from Wilson et al. 2015 and Wolf et al. 2020 are interesting. I would like to see a little more exploration of the oceanographic reasons as to why the results from this study (from the Arctic) do not follow the same patterns as those from Wilson et al. and Wolf et al (from the tropics).
    a. For example: were the average rates of primary productivity, and therefore perhaps the organic content of the seawater, higher in the tropics? And if so, could this help to explain the observed higher n_S values for the seawater from Wilson et al.'s and Wolf et al.'s analyses? This could be easily explored by comparing satellite retrievals of surface chlorophyl-a concentrations.

4. The authors propose that the ice nucleation measurement technique might contribute to the differences between their results and the results of Wilson et al. and Wolf et al. Specifically, the authors suggest that the differences in temperature and relative humidity trajectories experienced by aerosol particles in the AIDA and CFDC techniques may impact ice nucleation behaviour. The discussion covering this (Section 4.4) is rather speculative. It could be strengthened with further citations and details on key points the authors touch on. I outline a few specific recommendations below:
    a. The authors should better reference the literature on temperature and relative humidity trajectories as particles enter CFDCs. For example, I recommend citing and discussing the results in Rogers, 1988, Garimella et al., 2016, and Kulkarni and Kok, 2012. These papers include simulations describing the T and RH trajectories experienced by particles as they enter the CFDC.
    b. Once the T and RH trajectories are better discussed, the authors should expand on how the differences between CFDCs and AIDA can lead to physical differences in particle water uptake. The authors should mention that the rates of water uptake through organic coatings can be estimated for model organics (e.g. Price et al., 2015; Renbaum-Wolff et al., 2013). These calculations, even if not yet possible for complex mixtures of marine organics, at least provide a theoretical underpinning for the types of issues the authors raise.
    c. The authors might expand on their call for an intercomparison by suggesting that part of the intercomparison could be to subject aerosols to various "precooling" trajectories, i.e., controlling the temperature and relative humidity of aerosols in a large mixing chamber (NAUA?), prior to CFDC sampling. This could help facilitate comparison between AIDA and CFDC data.
    d. The manuscript is already quite long, and I do not mean to require that the authors add much text in response to the above points. Two or three sentences for each point should suffice.

Minor Comments
Abstract

5. Line 16: "*Only a small fraction of sea salt aerosol is transported to the upper troposphere...*" Please change "sea salt aerosol" to "sea spray aerosol," since these aerosol particles are often internally mixed and compositionally complex, consisting of more than just salts.

6. Line 22: "*The particles were suspended in a large cloud chamber...*" I think it would be useful to specifically mention AIDA here.

7. Line 32: "*we also discuss how far instrumental parameters...*" Semantical point, but I feel you don't discuss "har far" – i.e., quantify the extent to which – these parameters might impact results. You only discuss that they could impact the results without supplying an estimate for how large the magnitude of the impact might be. I would remove the word "far."

Introduction

8. Line 44: "…*homogeneous freezing of pure water droplets, which takes place below about 235 K.*" Please cite Koop et al. 2000 here, or your reference of choice.

9. Line 63: "…*the freezing data are usually reported as the temperature-dependent number of INPs per either droplet volume or volume of collected air.*" Temperature-dependence is reported for INP concentrations in the mixed-phase cloud regime; but in the cirrus regime below liquid water saturation, INP concentration is reported as a function of both temperature *and* relative humidity. Please clarify this in the text.

10. Line 78: "…*showed contributions of up to 25% from sea salt over ocean regions.*" Please change to "over ocean <u>and coastal</u> regions."

11. Line 81: "…*if we are to explain regional indications of heterogeneous ice nucleation activity...*" I'm not sure I understand the meaning of the word "indications" here. Perhaps change to "importance" or "impact" or "variability?"

12. Lines 155-158: Can the authors clarify what is meant by "partial deliquescence" or "before full deliquescence?" Do they refer to pre-deliquescence uptake of water (i.e., hygroscopic growth below the DRH)? Or do they refer to the time between the start of deliquescence and full deliquescence above the DRH?

13. Line 166 and throughout: I think "*Emiliana huxleyi*" should be spelled "*Emilian**<u>ia</u>** huxleyi*."

14. Line 174 and throughout: I think "*Perchlorococcus*" should be spelled "***<u>Pro</u>**chlorococcus.*"

Experimental

15. Line 283: "…*particles generated by nebulising the undiluted microlayer and surface seawater samples*…" were the samples homogenized (e.g., shaken) after thawing and prior to aerosolization?

16. Line 318: "*For a subset of samples, we diluted the suspensions by a factor of 10 and 100 with ultrapure water to extend the measured $n_{INP}(T)$ spectrum to lower freezing temperatures*." At what temperatures was this extra dilution step necessary?

17. Line 342: "*…we calculated the ice nucleation active surface site density, ns, with an estimated uncertainty of* ± *40%*." This uncertainty range seems rather large. Can the authors briefly summarize here the factors that go into calculating uncertainty in n_S?

18. Line 345: "*…we consider the extreme scenario…*" Is this considered "extreme" because experimental experience demonstrates that counting frequency is typically much higher?

19. Lines 346-349: This is a nice description of lower limits!

Results

20. Line 362: "…*corrected for the freezing point depression by the salts*." Can the authors provide more description, or a reference, as to how this was freezing point depression correction was done?

21. Line 373: "*This may be partly explained by the weather conditions...*" E.g., high winds? Can the author provide a typical wind speed during these measurements? The authors might reference one of the numerous studies indicating the wind speed at which the microlayer breaks up, e.g. Wurl et al., 2011.

22. Line 409: "…*any observable heterogeneous ice nucleation mode must be related to the organic material contained in the aerosol particles because the inorganic salt components are not yet ice-active at this temperature.*" Is it not also possible that the seawater also contains dust? See e.g. Cornwell et al., 2020.

Discussion and Outlook

23. Line 574: "…the processing of exudates either through biological processes such as microbial metabolism or physicochemical processes…" Please add a reference to support this discussion of microbial metabolism. I suggest either McCluskey et al., 2017 and/or Wang et al., 2015, but feel free to add another.

24. Line 583: "However, the amount of dispersed ice-nucleating entities was obviously much smaller than in the Wolf et al. (2019) study." Please state whether the cell concentrations were similar or different between this study and Wolf et al.

25. Line 628: "…where the bursting of bubble cap films can lead to the formation of highly organically enriched particles." Please add a reference.

26. Line 631: "…*the ice nucleation mode might change from immersion freezing, as observed in the AIDA experiments, to deposition nucleation, where ice formation initiates by the deposition of water vapour on crystalline or glassy surfaces*." Please add a reference (or two) that discusses depositional freezing on glassy organic aerosols. E.g. Murray et al., 2010.

27. Line 673: "Its transit time through the nucleation region of a CFDC is typically about 10 seconds." Please add a reference for this residence time. E.g. Garimella et al., 2016.

Figures and Tables

Table 1: Be sure to correct the spelling of the names here, as indicated above.

Table 2: What does the uncertainty or variability in the mean diameter (±0.05 μm) represent?

Works Cited

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