ACP Response to RC1 for *Low Temperature Ice Nucleation of Sea Spray and Secondary Marine Aerosols under Cirrus Cloud Conditions*
Format: The reviewers' comments are quoted in italics
Line number in the response refers to the revised manuscript with tracked changes.
Quotation in red color stands for revised/added text in the revised manuscript
Responses in blue

General comments
In this paper, the authors present their findings on the ice-nucleating particle (INP) characteristics of the Sea Spray Aerosol (SSA), which were generated from a Marine Aerosol Reference Tank (MART). Additionally, the researchers explored the impact of atmospheric aging on these characteristics. Interestingly, they found no observable effect of the atmospheric aging. On the whole, the study is methodologically sound. However, I must express three major concerns as well as a few specific issues related to the content, which I will delve into more deeply below. Despite these concerns, the study remains intriguing and offers valuable contributions to the broader scientific community's understanding of the INP characteristics of SSA. There is no doubt that with necessary revisions, the work will be worthy of publication. Nonetheless, it is imperative to note that major revisions are required to elevate the study to its full potential.

We would like to start by thanking the reviewer for their thoughtful comments and contributions to this manuscript. We will address both the major and minor below.

Three major issues:
1.The freezing mechanism at temperature < 220K
The elucidation of the nucleation mechanism in SSA remains a significant and yet unresolved scientific query. The authors of the current study, intriguingly, appear to circumvent direct discussion of the low-temperature nucleation dynamics of SSAs. They opt instead to vaguely encapsulate the complex phenomena using the generic term 'heterogeneous freezing.' The data put forth in this paper, particularly as illustrated in Figure 5, presents a compelling view. It appears to document a transition from homogeneous to heterogeneous nucleation as temperatures descend towards 220 degrees. Nucleation observed under these chillier conditions within a range spanning from water to ice saturation. This behavior should ideally be defined as deposition nucleation, however, Figure 5 sheds light on the temperature interval wherein the pore condensation freezing (PCF) manifests itself. A striking alignment is observed between the nucleation occurring below 215 degrees and the PCF. This concurrence seemingly substantiates the notion that SSA nucleation under colder conditions could indeed be characterized by the PCF.

The pathways of heterogeneous nucleation were not resolved in this study or Patnaude et al., (2021). However, based on the recommendations of multiple reviewers we have added additional background on the dominant freezing pathways discussed in previous studies in the Introduction, and have inferred the immersion freezing pathway as the most likely heterogeneous freezing mechanism in this study as discussed in the Results section 3.2. and Conclusions.

L117-L129: "In Patnaude et al. (2021) we posited that our ice nucleation results for simpler model SSA were a result of the competition between full deliquescence and immersion freezing. Those freezing results at temperatures > 220 K were characteristic of homogeneous freezing, in agreement with other previous studies (Schill and Tolbert, 2014; Wagner et al., 2018), which was likely due to the full deliquescence of the salt components around ~75 % RH_w, as defined by Tang and Munkelwitz, (1993) that occurred prior to the onset of immersion freezing. Below 220 K, SSA particles have been found to initiate heterogeneous nucleation at/near the range of deliquescence relative humidities (DRHs) for NaCl and SSA. Both Schill and Tolbert, (2014) and Wagner et al. (2018) concluded that at temperatures below

220 K, the phase state of their SSA particles was characterized by a solid core with a brine layer shell, and speculated that heterogeneous freezing proceeded via the immersion pathway. Patnaude et al. (2021) further discussed the reason for the transition between homogeneous and heterogeneous pathways around 220 K, which also happened to occur at the intersection of the DRH and PCF freezing parameterization from Marcolli et al. (2014) for a specific pore size. However, due to the lower DRHs for the additional salt components such as magnesium and calcium (Tang et al., 1997) the PCF pathway is less likely. The exact heterogeneous freezing mechanism of SSA and cause of the transition between freezing pathways remains unresolved."

L720-L734: "Similar to Patnaude et al. (2021), the pathway for heterogeneous nucleation and the transition between homogeneous and heterogeneous below 220 K remains unresolved. Deposition freezing remains an unlikely freezing pathway for pSSA and aSSA+SMA (at 1 % frozen fraction) at/near the DRH as water uptake of minor salt constituents would begin at lower RHs (Schill and Tolbert, 2014; Tang et al., 1997; Wagner et al., 2018). The competition between full deliquescence and immersion freezing or PCF to explain this transition in freezing pathways was also discussed in Patnaude et al. (2021) but bears repeating. While the 1% frozen fraction of both pSSA and aSSA+SMA occurred at near the PCF line, we do not believe this to be the likely freezing pathway for two reasons: 1) the PCF line shown in Figure 6 was approximated for an 11 nm pore size, and there is little evidence this is an realistic size for SSA and 2) the SSA particles would need to be fully dry to retain surface pores, which was not likely the case at 75 % RH_w where 1 % frozen fraction occurred. At temperatures above ~220 K, particle deliquescence would occur at a lower RH_w than the expected value for immersion freezing (see Patnaude et al., (2021) Figure 8), thus favoring full dissolution and homogeneous nucleation at much higher RHs. At lower temperatures (< 220 K), the particles may have developed a brine layer, which has been observed in two previous studies (Schill and Tolbert, 2014; Wagner et al., 2018), and ice nucleation may have proceeded via the immersion pathway. Therefore, the most likely heterogeneous freezing pathway for pSSA and aSSA+SMA was immersion freezing."

L766-L767: "Based on the similarities between freezing results in this study and Patnaude et al. (2021) and Wagner et al. (2018), the dominant heterogeneous freezing mechanism below 218 K was likely the immersion freezing pathway."

2.The phase state of the SSA
The main objective was to compare the INP characteristics of the pure and aged SSA, however, the reviewer was concerned the state of particles could influence the results. In this study, the measurement of humidity was performed before the coil cold trap, maintaining a controlled relative humidity at 10% under ambient temperature conditions. However, this level of water vapor pressure can escalate from a few thousand to tens of thousands supersaturation with respect to ice at 220K. Consequently, it is imperative for the authors to consider the dwell time within the coil cold trap and the Continuous Flow Diffusion Chamber (CFDC). Furthermore, it would be beneficial to generate estimations of the phase state prior to its entry into the CFDC.

The particles were further dried by a molecular sieves drier after the RH monitor described in the previous sentence. Additionally, they passed through a coil cold trap that was immersed in the inner wall cold trap. This chilled and dried the particles to nearly 0 % before entering the CFDC column. We have added a sentence to make this clearer.

See our response to your comment on phase state of organics below.

L211-L213: "Prior to particles entering the CFDC they passed through a coil cold trap immersed in the inner wall chiller, which further chilled and dried particles and incoming sample air to a frost point at

least 5 K below the CFDC measurement temperature, corresponding to an ambient temperature RH of ~0 % (see Kasparoglu et al. (2022)).”

3. The setup of the experiment
Currently, the sample air directly enters the oxidation flow reactor after exiting from the MART instrument. It is suggested that the sample air should be dehumidified before passing through the oxidation flow reactor. This is because, during liquid-phase oxidation, the crystallization of SSA solution droplets into crystals may not affect its surface structure. However, if oxidation occurs in the solid phase, the pores on the surface of the SSA particles might be filled, thereby affecting its ice nucleation properties.

As mentioned in the text, it was intentional to keep the air somewhat humidified in order to control the oxidation chemistry in the OFR, and to maintain consistency with previous SSA experiments (Prather et al., 2013; Mayer et al., 2020b; DeMott et al., 2023). We have added an additional sentence to clarify the oxidation reactions that occurred would mimic those that occur in the boundary layer of the atmosphere, and that this may be relevant for impacts on ice nucleation. Further studies would be needed to explore oxidative impacts occurring for upper tropospheric (very dry) conditions. We may also note that we have added substantial discussion to the paper regarding expected alteration of organics based on similar prior studies that included compositional measurements, in response to comments from other reviewers.

L204-L205: “Because the air was humidified inside the OFR, the oxidation reactions that occurred would mimic those which occur in the marine boundary layer.”

L784-L800: “2) the air stream remained humidified when entering the OFR and the pSSA particles were thus likely in an aqueous state. Whether oxidation of their organic content could proceed in the wetted or partially wetted state, and whether changes to the pSSA organic content would be similar to that observed when processed in a dry crystalline state is unknown, or 3) the addition of SMA coatings to the pSSA and/or alteration of organic components of the pSSA did not alter the crystallization behaviors, nor did they hinder the water uptake by the inorganic salts.”

Specific comments:

P1, Line 16: I suggest use the supersaturation with respect to ice instead of RH to evaluate the onset of the ice nucleating forms.

This statement in line 16 is in reference to Figure 6, which uses RH_w. Because homogeneous nucleation is driven by the condensation of liquid water, we believe that RH_w gives greater insight into nucleation processes than ice supersaturation (where homogeneous freezing onsets are more variable as a function of temperature).

P3, Sec 2.1: The artificial seawater was filter through a TOC+HEPA filter to remove the insoluble particles, what about the natural seawater? There might be some dust and biological particles inside the natural seawater which have influence on the INP measurement.

We did not filter the natural seawater because we wished to retain any biological particles that were present in the water. This was standard protocol for all previous ice nucleation studies in the literature (references already included), when using real seawater. We have added an additional statement that the seawater was not filtered.

L171-L172: “Unlike the ASW, the SW was not filtered before being added to the MART in order to retain biological material.”

P5, Line 151-152: I was wondering why there were so many particles during the "blank experiment" with DI water. Does that mean there were contamination of the MART and sampling tubes? Thus, I strongly suggest do "blank experiment" before and after each experiment.

The blank experiments were conducted with the DI water at room temperature rather than being chilled, and exposing any gaseous species present to oxidation in the OFR. The blank experiment took place during the one day we had between the experiments with the ASW and SW, as the SW arrived and needed to be added into the MART immediately after delivery. It is discussed in the text that the reason for the high particle concentrations during this test was likely due to higher VOC emissions from the MART (acrylic) at warmer temperatures than occurred in the tests with chilled water. We leak checked the entire system after adding the DI water to the MART, and measured no particle emissions with the OFR off, therefore we do not believe it was contamination in the sampling tubes.

It would not have been possible to perform a blank test before and after each experiment due to the limited time we had with borrowed equipment because it took significant time to drain/fill the MART, which also had to be cleaned before and after changing out the water.

P5, Line 155: TSI models 3080, remove the 3081 and 3010, which is the model of DMA and CPC.

The SMPS system consists of a classifier, DMA, and CPC, which are the three model numbers given. The 3080 by itself is just the classifier, not a functional SMPS. There likely is a TSI model number that corresponds to the collection of these three pieces, but it is no longer easily searchable and hence not useful to use in the manuscript.

*P5, Line 160: This paragraph is confusing and very hard to understanding.*

See response to RC2 regarding this paragraph. We hope those changes have clarified this section sufficiently.

Line 195-295, when discussing the influence of organics, some studies (Ignatius, et al., 2016; Knopf et al., 2018; Tian et al., 2022) found organic aerosol (likely secondary) could be glassy (Koop et al., 2011) and efficient heterogeneous ice nuclei under the condition of low RH, which could be referenced to support the point that organics itself may serve as INP.

Thank you. We have added some discussion on the potential of a glassy phase state of the organic particles in both the Introduction and section 2.2:

L137-L146: "The inclusion of additional organic components in primary SSA may have implications for ice nucleation both below and above 220 K. Clearly, organics from seawater that are contained in primary SSA, and/or those added to the aerosol through atmospheric processing of SSA, are responsible for a major proportion of the ice nucleation activity of SSA in the mixed-phase cloud regime (McCluskey et al., 2018a), and a question has remained as to how effective these organics are as INPs below 238 K. Organic aerosols have been shown to form a glassy state under cirrus cloud conditions (Berkemeier et al., 2014; Ignatius et al., 2016; Knopf et al., 2018; Koop et al., 2011; Murray et al., 2010) and depending on the glass transition temperature and DRH, these particles may have heterogeneous ice nucleating ability at temperatures > 220 K, where the salt components of SSA would have already dissolved. It is unknown how organic rich particles would compete with the salt components of SSA below 220 K, but based on the results in Kasparoglu et al. (2022), the contribution of glassy SOA may be relatively minor."

L249-L258: "It is assumed that particles generated from SW contain high fractions of insoluble organic particles or salt particles mixed with organic carbon below 500 nm, similar to previous lab-generated SSA (Prather et al. 2013; Bertram et al. 2018; Kaluarachchi et al. 2022a). In addition, DeMott et al. (2023) showed particle morphologies of laboratory-generated SSA that include organic coatings in the submicron size range, both before and after similar use of an OFR for oxidation studies. The MART was demonstrated to produce substantially similar size distributions and SSA compositions compared to a more natural wave breaking process for bubble bursting (Prather et al., 2013; Stokes et al., 2013), so no bias in organic content in comparison to natural SSA production is expected. During cooling, the RH_w would be low enough such that organic particles or coatings may form a glassy state (Ignatius et al., 2016; Knopf et al., 2018; Koop et al., 2011), as shown by the shaded green region in Figure 2, which represents the glass transition conditions for sucrose (Zobrist et al., 2008)."
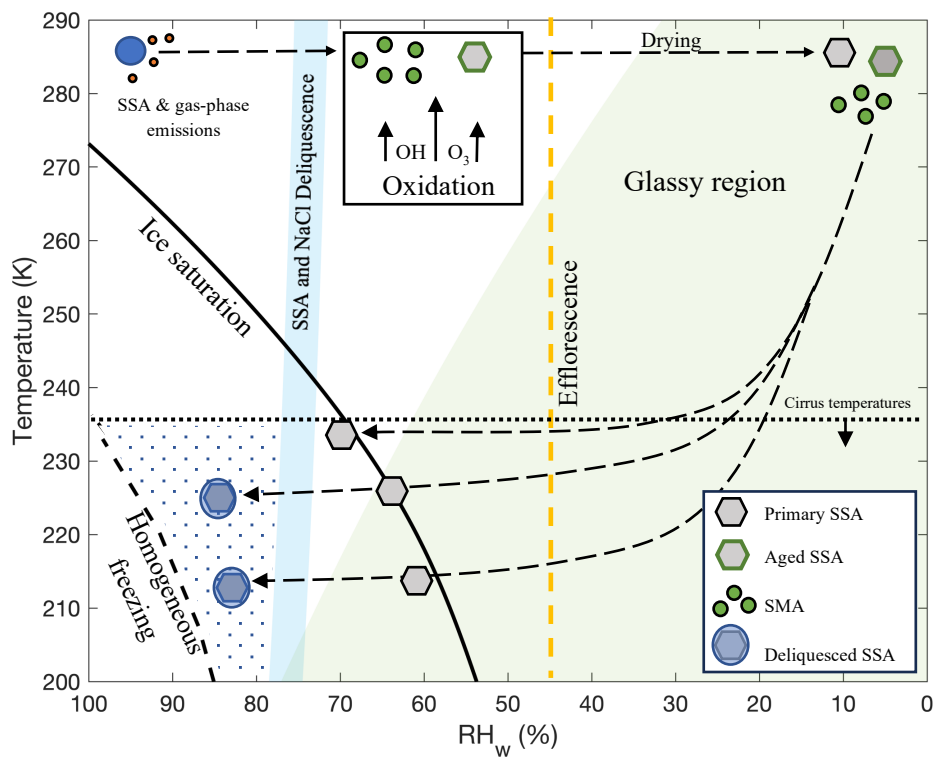
Figure 2. Expected trajectory and phase state of the pSSA, aSSA+SMA and SMA particles for CFDC experiments, modified from Patnaude et al. (2021). Orange dashed line is the expected efflorescence line for NaCl on the basis of the parametrization of anhydrous NaCl and extrapolated to cirrus temperatures (Tang & Munkelwitz, 1993). The blue shaded region represents the range of possible deliquescence RHs for NaCl and SSA, using the parameterization from Tang & Munkelwitz, (1993) for NaCl extrapolated to colder temperatures as the upper bound and shifting it down 4 % RH_w for SSA similar to Wagner et al. (2018). The long dashed black lines follow the path of aerosol particles through drying, cooling, and CFDC scans at different temperatures. The blue circles represent aqueous solutions, gray hexagons represent effloresced pSSA aerosols, and the light blue circles with embedded hexagons represent fully deliquesced particles. The gray hexagons with green outlines and green circles represent the aSSA+SMA and SMA particles, respectively. Lines indicating ice saturation and predicted homogeneous freezing conditions are also denoted. The dotted region represents conditions where aerosol particles experience ice supersaturated conditions and relative humidities that exceed their deliquescence point. The green shaded region represents conditions below the glass transition curve of sucrose from Zobrist et al. (2008).

P7, Sec2.4: The IS show the mixed phase regime (-38–0 °C) INP concentration which inconsistent with the main theme of this study, and the results was shown in the supplement. The author need to carefully consider whether to retain this section of content.

We see the reviewer's point, that these data are outside the temperature regime being focused on. We have decided to remove this section from the manuscript as we also removed the supplemental figure S3 that included the ice spectrometer INP spectra (see response to RC2).

References:

Koop, T., Bookhold, J., Shiraiwa, M., Pöschl, U. Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere. Phys. Chem. Chem. Phys., 2011, 13, 19238-19255.

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Ignatius, K., Kristensen, T. B., Jarvinen, E., at al. Heterogeneous ice nucleation of viscous secondary organic aerosol produced from ozonolysis of α-pinene. Atmos. Chem. Phys., 2016, 16, 6495-6509.

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Zobrist, B., Marcolli, C., Pedernera, D. A. and Koop, T.: Do atmospheric aerosols form glasses?, Atmos. Chem. Phys., 8(17), 5221–5244, doi:10.5194/acp-8-5221-2008, 2008.