Review of “Sublimation of frozen CsCl solutions in ESEM: determining the number and size of salt particles relevant to sea-salt aerosols” submitted to ACP by Vetráková et al.

Reviewer #1

This study presents sublimation of CsCl solution to elucidate formation of fine salt particles and potential as origins of sea-salt aerosols in polar areas. This unique approach can provide us very interesting and important suggestion about sea-salt aerosols in polar areas. There are several interesting conclusions obtained from this study based on laboratory experiments using ESEM:

1) Fine salt particles formed through sublimation of salt solution under colder conditions.

2) Size and number concentrations of salt particles related to temperature and the concentrations of salt solution.

Overall, this topic and subject is suitable for scope of ACP. I am confident that this investigation has potential to demonstrate these interesting results. However, I found some weakness in the manuscript. Hence, I recommend major revision before publication in ACP. My specified suggestions and comments are listed below.

Thank you very much, we really appreciate you consider our study interesting. In the following text, we reply to your comments and answer the questions. We are currently working on implementing the suggested changes into the manuscript.

Major comments

1. Application of laboratory results to ambient conditions

In this study, sublimation processes were examined under several artificial conditions such as non-seeding, seeding, and LN frozen. Although I understand different conditions between laboratory experiments and fields, more careful discussion are required for robust conclusion. Specifically, authors need to discuss carefully whether the examined artificial conditions are available in polar areas, and what the most usual conditions are in polar areas. For example, there are a large amount of brine on younger sea ice. Actually, the wet surface is present on sea ice even below -20 °C (e.g., Hara et al., ACP, 2017). Therefore, “the edge” might not be realistic in such conditions. On the other hand, salinity of snow on the aged sea ice and multi-year sea ice are lower than that on the younger sea ice, as discussed in this study. However, I am not sure whether “brine” is present in the snow the aged sea ice and multi-year sea ice, or not. Is that available? At least, the snow on the aged sea ice and multi-year sea ice were not wet, as far as I observed that visibly.

Complete freezing of brine is a matter of brine composition and temperature. In our experiments, the eutectic temperature of CsCl brine lies close to −23 °C; below this temperature, brine solidifies (except for the effect in chapter 3.3). However, natural seawater contains versatile ratio of diverse salts and its eutectic temperature depends on particular way of freezing: -54 °C for Ringer-Nelson-Thompson pathway or -36 °C for Gitterman pathway (Gitterman 1937, Vancoppenolle et al. 2019). Therefore, the limit of −25 °C presented in this study (and valid for CsCl) will not be sufficient for the sea salt. However, the temperature of -36 °C, which may be sufficient for solidification of the sea salt brine according to the Gitterman pathway, is often reached in polar areas.

Our experiment result is likely more appliable to the newly formed sea ice surface or with snow on top of it where high salinity is observed. However, on aged sea ice and multi-year sea ice, snow salinity is low and salts are mainly from transported saline particles generated from nearby open leads, polynyas or even open ocean, rather than from bottom interface of the sea ice via upward wicking process (Domine et al., 2004). Therefore, salts are mostly dry not wet in multi-year ice snow, which means the formation process of salt particles from low salinity snow particles may be different from what we observed in this experiment.

The low salinity experimental result may apply to metamorphosed ices; the change of temperatures via a short period of warming or even through the absorption of solar energy due to the existence of impurities such as black carbons and dusts may melt snow (Warren 1984; Kang et al., 2020) and cause a wet brine pond.

Another natural condition under which the sea water of various concentration is freezing embodies in the refreezing of partly melted sea ice. The “wetness” of the snow is given by the salt concentration, its distribution in the medium and the temperature.

2. Seeding

When solid materials are present in brine (i.e., seeding in this study), salts can be crystalized or precipitated on the solid materials. In this study, small ice crystals were used as “seeding” materials. Considering brine is attached to ice under ambient conditions on sea ice and in snow, “seeding” conditions are real situation. Or not? Which are realistic conditions (non-seeding or seeding) which authors considered. Additionally, upside surface of brine on sea ice and snow is attached usually to colder air in polar areas in contrast to colder surface in the bottom (i.e., cool stage) during the laboratory experiments. More careful explanation and discussion are required.

Certainly, heterogenous nucleation by solid particle can trigger the crystallization of a supercooled or (over)saturated solution. In here, we apply ice crystals to trigger the ice crystallization. In the natural arctic conditions brine can appear on the sea ice and snow after its partial melting or flooding of the surface. Then, depending on the climatic conditions such as temperature drop and amount of precipitation, both the spontaneous and seeded freezing can occur. We propose the “seeding” condition is more common than the “non-seeding” condition in the Arctic even though we are not aware of relevant literature. There are numerous items in the polar winter atmosphere that can materialize the seeds, e.g., ice crystals (diamond dusts), drifting or blowing snow particles as well as various natural particles (e.g. dust) and pollutants (e.g. black carbons).

In the polar areas, surface snow or brine exposed to the air on sea ice usually face much colder temperatures than the bottom parts. In the laboratory experiments, only the bottom of the sample is cooled directly by the stage during the freezing phase (the specimen chamber is open to atmospheric conditions). However, the frozen samples are much smaller in comparison with natural ones, therefore we expect only small temperature differences across the sample. In our seeding procedure, the samples are thermally equilibrated prior to seeding, and the seeding crystal is put onto the surface, so we believe the sample freezes from the top, similar to the natural sea ice. On the other hand, the non-seeded samples in our experiments are more likely to freeze from the colder bottom.

When the specimen chamber is closed and evacuated, the gas inside the chamber becomes colder due to its expansion, and the sample surface is cooled via sublimation, too. In this phase of the experiment, the sample surface may become colder than the bottom part. Still, due to the small sample size, we don’t expect large temperature gradients.

3. Evaporation and sublimation

Laboratory experiments showed clearly that many salt particles are observed on the substrates after sublimation and evaporation. This result is very interesting. Crystallization of the salt particles are found on the dry surface on the substrates where brine was absent via brine shift and sublimation as shown in Figs. in the manuscript. The dry surface might be not available under the conditions with presence of brine on sea ice and snow in polar areas.

We agree with the reviewer: there are hardly any dry surfaces in the Arctics. Nevertheless, the observation of the salt particles formation in the microscope is relevant to the natural conditions as the produced particles would fall down to the underlying snow or ice or will be airborne within the sublimation process.

1. Size and size distribution

In this study, maximum diameter is used as particle size. As shown in ESEM images, the morphology of salt particles was irregular not spherical. I understand the difficulty to measure the size of salt particles with irregular shape. However, more careful procedure to measure the size is required, for example, to measure minimum diameter and mean diameter. Also, variations of size distribution of maximum diameter, minimum diameter, and mean diameter should be discussed.

Thank you for your comment. We agree the maximum diameter of particles of irregular shape is not an ideal parameter. We have modified the histograms in Figure 12 and used an equivalent diameter instead. The equivalent diameter expresses the diameter of the disk whose area is equal to the area of the particle. Also, we newly added more parameters related to particle sizes (equivalent, maximum, minimum, and mean diameter) into a statistical summary presented in table S2 in SI.

Specific comments

1. Line 187-189: Add information of Fig. No which you show.

Although we usually show already sublimated samples in the results, during the experiments we observe whole sublimation of frozen solutions and we are able to recognize if the brine is in liquid state or it solidified. In the presented figures, the solidified salt on the ice surface is nicely visible in Figures 11 and 17a,d,g.

Following text was added:

(the solidified salt on the frozen surface is nicely visible e.g. in Figures 11 and 17a,d,g).

2. Line 226-227: Size distribution of salt particles by non-seeding and seeding

“Seeding” preferred to form smaller (aerosolable) salt particles in this study. What are reasons of this different? More discussion is useful for readers.

The reasons for this behaviour can be explained by examining the micrographs of the solutions frozen without seeding and with seeding (Figure 2 in Vetráková 2019) and micrographs of the appropriate sublimation residua at both discussed concentrations (Figure 7 and 8 in the current manuscript). The explanation lies in the freezing directionality and rate. With the seeding, the sample freezes slowly at low degree of supercooling forming larger ice crystals (Table 2 in Vetráková 2019). In contrast, non-seeded samples freeze faster (ca 150 mm/s) and directionally from the bottom up; such a process results in larger amount of salt on the surface. Micrographs show clearly (Figure 7 and 8), that in seeded samples the salt remained mostly in the veins finally forming regular geometrical patterns after the ice sublimation, whereas the non-seeded samples allowed mostly the larger particles originating in the triple junctions, pools and on the ice surface.

Section 3.2: LN-frozen and full sublimation

LN-frozen samples were simulated with the complete freezing condition. Difference between LN-frozen samples and the other samples is very interesting to understand formation of small salt particles depending on freezing processes under the colder conditions. However, I wonder whether the complete freezing of brine can proceed in polar areas, particularly where sea-salt aerosols are released. As well as, I am not sure that full sublimation occur on the surface under the conditions with presence of brine. Add more careful explanation and discussion.

In the manuscript, the LN-freezing experiments are present mostly to show the large difference between “natural” conditions (spontaneous freezing and seeding) and laboratory freezing in LN. Moreover, LN temperatures are relevant for extraterrestrial bodies. Complete freezing of brine is a matter of brine composition and temperature. In our experiments, the eutectic temperature of CsCl brine lies close to −23 °C; below this temperature, brine solidifies (except for the effect in chapter 3.3). However, natural seawater contains versatile ratio of diverse salts and its eutectic temperature depends on particular way of freezing: -54 °C for Ringer-Nelson-Thompson pathway or -36 °C for Gitterman pathway (Gitterman 1937, Vancoppenolle et al. 2019). The temperature of -36 °C is often reached in polar areas. In our experiments presented in Zavacka (2022) we observed the differences between the sublimation at -30 and -40 °C indicative of remaining liquid at higher temperature.

At low temperature (solidified brine) full sublimation is not needed for the release of salt particles. Small salt particles are released continually as the ice sublimates.

1. Section 3.5: Surface conditions of sea ice with brine and snow

In this section, implication to polar atmosphere and conditions was mentioned and discussed. Surface conditions in sea ice areas changed drastically depending on presence of brine, sea ice growth (aging), accumulation of snowfall, and so on, as shown by Hara et al. (2017). Similar to sea ice conditions, snow salinity (i.e., sea-salt concentrations) on sea-ice is varied largely by blowing snow and snowfall. Therefore, I strongly recommend that formation of aerosolable salt particles is discussed on every (or typical) surface conditions such as wet surface on younger sea ice by brine, conditions with presence of frost flower, wet saline snow on sea-ice, and low – middle saline snow on sea ice (aged seasonal sea ice or multi – year sea ice). Although some explanation and discussion were mentioned already in the manuscript, correspondence between laboratory results and the ambient conditions in the polar areas was interpreted hardly because of partly confusion.

The frost flowers and young sea ice with salt concentration above 35 psu are unlikely direct sources of SSA at any temperature. However, dilution of the salt and the presence of the ice and snow with concentration below 8 psu (as is typical of saline snow on sea ice) make the formation of SSA feasible especially at low temperature.

Line 367: Temperature of mirabilite precipitation

Add reference which show the temperature of -6.4 °C.

The reference was added to the text.

When the ice temperature ranges below −6.4°C, which is a typical situation in a polar winter and spring, mirabilite ($Na_2SO_4 \cdot 10\ H_2O$) starts to precipitate out from the brine (Butler et al., 2016a, 2016b), ...

Line 369-373:

Changes of surface conditions of sea-ice were shown in Hara et al. (2017).

Hara, K., Matoba, S., Hirabayashi, M., and Yamasaki, T.: Frost flowers and sea-salt aerosols over seasonal sea-ice areas in northwestern Greenland during winter–spring, Atmos. Chem. Phys., 17, 8577-8598, https://doi.org/10.5194/acp-17-8577-2017, 2017

Thank you for the suggestion, we added the reference to the text.

Sizes of small salt particles shown in this study ranged in micrometer or larger than 10 mm. It is true that particles with size of micrometers are "aerosolable". However, these particles may be attached to the surface of ice and snow in polar regions. What are specific processes to release sea-salt aerosols into the atmosphere? Because of less volatility of sea-salts, sea-salt aerosols must be released through the physical processes such as erosion during the strong winds and then sublimation. Although release of salt particles with size of micrometers can be explained by the processes, sea-salt aerosols in the Antarctic were distributed in smaller than 1 mm (Yang et al., 2019; Frey et al., 2020) and smaller than 100 nm (Hara et al., 2011). If possible, these issues should be discussed.

We performed most our experiments using the resolution of 0.5 µm, which enabled us to get a full picture of the related processes. When more detailed pictures were recorded, we also observed smaller particles, but we are not able to evaluate their number and size due to lack of statistically relevant data.

References:

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