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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaporating brine from frost flowers with electron microscopy, and implications for atmospheric chemistry and sea-salt aerosol formation" *by* Xin Yang et al.

Anonymous Referee #1

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This manuscript, as reflected in the title, addresses relevant scientific questions concerning the role of frost flowers (FF) in sea-salt aerosol (SSA) formation. The novelty of the research mainly relates to the use of an Environmental Scanning Electron Microscope (ESEM) to investigate frost flower dynamics in-situ. The works presents results from experimental temperatures of -5.2 and -17 °C, though further experiments at -10 and -12 °C were completed but not detailed in the manuscript. The most substantial conclusion reached outlines that FF's are not a direct source of SSAs, which is consistent with previous suggestions based on wind tunnel measurements (Roscoe et al., 2011).

The scientific methods and assumptions are clearly outlined, with exception to the use

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of a binary NaCl-H2O system in preference to seawater. The experiment descriptions are appropriate for allowing reproduction by fellow scientists. Generally the results are sufficient to support the interpretations, although the discussion of snow particles in section 5.2 is not strictly relevant to the frost flower observations presented. For this reason I suggest removing the first two paragraphs on page 9 (detailed below) and combining sections 5.1 and 5.2. There could also be a greater level of discussion about how, if frost flowers are not a source of SSA's, then why are winter peaks observed with measured [SO42-/Na+] ratios lower than that of seawater?

The authors do provide proper credit to related work with an appropriate quality and quantity of citations and references. The manuscript could benefit from inclusion of more references from literature concerning sea ice brine geochemistry, which would add interdisciplinarity whilst increasing the potential audience.

The abstract provides a concise and complete summary of the manuscript and the presentation throughout continues to be well structured and clear. Generally the language is fluent and precise, however some sentences would benefit from rewording (detailed below).

Mathematical formulae, symbols, abbreviations and units are correctly defined with exception of the use of ANSYS in the caption of figure 2. Lastly, the supplementary materials are an excellent addition to the manuscript. Specific comments

SECTION 1: Introduction

Page 1, line 31: "Outer space" is not relevant to this investigation. Remove.

Page 1, line 34: "Assessing the reactivity" of what?

Page 1, line 40: "Climate index" could instead be "paleo-proxy".

Page 1, line 43: Specify that the "distance to open water" is for polar environments that experience sea ice formation during winter.

Page 2, line 9: It may be beneficial to introduce the source of the brine by describing the sea ice brine system (see Light et al., 2003, Effects of temperature on the microstructure of first-year Arctic sea ice, JGR).

Page 2, line 10: Out of curiosity, why is SO42- removal inapplicable to sea spray? If sea spray is comprised of seawater aerosol particles that are subjected to sub-zero atmospheric conditions, why couldn't mirabilite precipitation occur on microscopic scales? I should stress that the manuscript does not need to be amended in relation to this comment.

Page 2, line 10: Experimental and model evidence has concluded that mirabilite can precipitate from sea ice brine at temperatures $\leq$-6.4 °C (see Marion et al., 1999, "Alternative pathways for seawater freezing", Cold Reg. Sci. Tech.; Butler et al., 2016, "Mirabilite solubility in equilibrium sea ice brines", GCA). The original estimate of -8 °C comes from Nelson and Thompson (1954, "Deposition of salts from seawater by frigid concentration"), with experiments not given sufficient time to attain equilibrium.

Page 2, line 17: This brine salinity is within the region of mirabilite precipitation shown in Butler et al., (2016, "The effect of mirabilite precipitation on the absolute and practical salinities of sea ice brines", Mar. Chem.).

Page 2, line 20: "high salinity" should be "high brine salinity". Furthermore, this sentence could be reworded with a more explicit description of the chemical reactions being referred to.

SECTION 2: Growth of the frost flowers and preparation of the samples

Page 3, line 5: The use of an aqueous solution of NaCl instead of seawater should be justified, with potential limitation of this method outlined.

Page 3, line 9: Can the quality of figure 1 be improved at all? At the moment it is a little hard to interpret.

Page 3, line 11: Remove "extremely".

SECTION 3: Environmental scanning electron microscope

Sections 2 and 3 both describe the methods of the investigation. I would therefore suggest creating a section 2 titled “Methods”, and then including the two current method sections as subsections (i.e. 2.1 and 2.2).

Page 3, line 37: Remove “material”.

Page 3, line 41: In the caption of figure 2, what is ANSYS?

SECTION 4: Results This section could be retitled “Results and discussion”.

Page 4, line 16: Remove brackets starting after “are”.

Page 4, line 18: I have noticed that in some cases a space is used before “°C”, and in others there isn’t a space. I would recommend including a space throughout.

Page 4, line 19: The way the sentence is worded at the moment makes it difficult to interpret. Is the viscosity of the brine nearly two times higher or two times lower than that of pure water? Also, what do the authors mean by ‘ambient’ temperature?

Page 4, line 20: Full stop on wrong side of reference.

Page 4, line 32: Amend citation for Buck (1981).

Page 4, line 33: Amend citation.

Page 5, line 6: Should “23.3 %” actually be 8.3 %? Also, with figure 4, I would suggest amending the x and y axis scales so that the experimental conditions of this investigation can be interpreted more easily.

Page 5, line 8: As a general thought, if equilibrium brine concentrations in frost flowers are maintained by ice melting, then the equilibrium composition of the brine within a frost flower should reflect that of sea ice brine inclusions at equilibrium. This just highlights an overlap between the study of frost flowers and sea ice brines.

Page 5, line 36: In relation to changing pH in sub-zero brines, Papadimitriou et al.

(2016, “The measurement of pH in saline and hypersaline media at sub-zero temperatures: Characterization of Tris buffers”, Mar. Chem.) or Rerolle et al. (2016 “Measuring pH in the Arctic Ocean: Colorimetric method or SeaFET?”, Meth. Ocean.) might be more relevant references.

Page 6, line 6: Explicitly refer to how this description is for experiments at -5 °C.

Page 6, line 18: Rather than “Apparently”, it would be better to relate this sentence to the NaCl-H2O phase diagram (figure 4).

Page 6, line 28: The manuscript seems to skip from S3 to S5. Is there an S4?

Page 6, line 36: Butler and Kennedy (2015, “An investigation of mineral dynamics in frozen seawater brines by direct measurement with synchrotron X-ray powder diffraction”, JGR: Oceans) would be a more suitable reference for the fast rate of hydrohalite dissolution upon warming.

Page 7, line 3: “thermodynamic conditions” should be “thermodynamic equilibrium conditions”.

SECTION 5: Atmospheric implications

I think that this section should become section 4.3, and the current sections 5.1 and 5.2 should become part of this (rather than being separate).

Page 7, line 35: Remove “concrete”.

Page 7, line 36: As this investigation is for the “general case of the ice-NaCl system”, the manuscript would benefit from a considered discussion about the limitations of using this binary system instead of seawater. According to the composition of standard seawater (Millero et al., 2008, “The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale”, Deep Sea Res.), Na+ and Cl- comprise 85.7 % of the total salt in seawater by mass. The remaining 14.3 % of solutes may play an important role in the geochemistry of frost flowers, particularly since

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mirabilite can precipitate from seawater when cooled below -6.4 °C.

Page 8, line 26: “condition” should be “conditions”.

Page 8, line, 42: If FFs are not a direct source of SSAs, then what theories are there for the winter maximums in SSA’s and the observation of [SO42-/Na+] being lower than seawater? The discussion here would greatly benefit from an appraisal of this.

Page 9, lines 1 – 15: I cannot see how these two paragraphs relate to the current investigation. Surely the study of SSA formation from snow and frost flowers requires two separate investigations? The discussion might be better of concentrating upon the topic outlined in the previous comment.

SECTION 6: Conclusions

Page 9, line 23 – 24: “This microphysical picture applies to not only the high saline FFs, but also the less saline snows, including blown ones”. I am not sure how this link is made, and how appropriate it is given that the measurements carried out in this investigation were solely on frost flowers.

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