

## **Reply to Referee #1 (Dr. Roscoe)**

We would like to thank your helpful comments to improve our manuscript. We responded to the general and specific comments. All comment are addressed in the revised manuscript. The updated parts by your comments indicates red words in the revised manuscript (pdf file). We separated Results and Discussion on basis of comment from Referee #2 (Dr. Dominé).

### ***Comment from Referee***

*A. Except for a couple of lines buried on p13, the authors ignore the discovery in 2008 and 2010, in field measurements and separately in laboratory measurements, that frost flowers can be of non-fragile structure not dispersed by wind, and in the laboratory not producing aerosol (Obbard et al. 2009, Roscoe et al. 2011). ...*

### **Reply from authors**

We agree with your comment. Description in “Introduction” and “Discussion” were modified as follows.

#### Introduction

Frost flowers are ice crystals containing brine and sea salts.

Frost flowers have a fine structure. Previous field and laboratory experiments indicated that frost flowers were less-fragile even under strong winds in spite of the fine structure (Obbard et al., 2009; Roscoe et al., 2010). In addition, model studies implied that blowing snow had significant contribution to atmospheric halogen chemistry (Yang et al., 2010; Abbatt et al., 2012; Lieb-Lappen and Obbard, 2015).

#### Concluding remarks

Under the conditions with strong winds, snowfall and blowing snow, snow particles were attached on frost flowers and slush layer. As suggested by laboratory experiments (Roscoe et al., 2010), aerosol particles are released insignificantly from frost flowers. However, Mg-rich sea-salt particles and Mg-salts are released from the brine and surface snow by winds.

Also, Yang et al. (2010) was added to the statements in the manuscript and “References”.

***Comment from Referee***

*B. There is no major scientific conclusion in the paper - it is an extensive and comprehensive report of the measurements and what they might mean in detail, but not what they might mean to Atmospheric Chemistry and Physics in general. Without resorting to a new set of work with a model, I doubt that there could be such a conclusion.*

**Reply from authors**

Thank you for your suggestion. We changed completely the description in “Concluding remarks”. From field evidences in this study and previous works, we proposed sea-salt cycles in the seasonal sea-ice area in “Concluding remarks”. We believe that our proposal (hypothesis) is useful and new set for sea-salt chemistry in the polar regions.

***Comment from Referee***

*1. Despite the text on p3 and elsewhere throughout the manuscript, we discover from Figure 1 that Site III is actually split into two. It would help if some reason for this was given, and if later text and captions said whether the result being described was from Site IIIa or IIIb.*

**Reply from authors**

Age of sea-ice at Site IIIa and IIIb was almost same, because the storm on 1 March, 2014 caused sea-ice breakage at sea-ice margin near Site III (blue line in Figure 1). We choose Site IIIa and IIIb as sampling sites near new sea-ice by traverse by dog-sledge team. Consequently, we denote both sites as “Site III”. From your suggestion, we used Site IIIa and IIIb in the revised manuscript. Descriptions about sea-ice conditions and sea-ice age were added to section of “2.1 Sampling sites and conditions”.

***Comment from Referee***

*2. The authors describe the good practice of storing brine samples in Japan frozen until analysis (p5 line11), but it seems that they were transferred to Japan unfrozen presumably because of the difficulty of carrying frozen samples by air. How long were the samples left unfrozen - 4 days, or several weeks?*

**Reply from authors**

The samples were kept below -20°C in Greenland and our laboratory. During the

transport from Greenland to Japan, samples were kept in “unfrozen” for ca. 3 days. The description was added to “2.2 Sampling of frost flowers, brine, snow and sea-ice”.

***Comment from Referee***

*3. It is also good practice to keep aerosol samples collected in polar regions frozen for shipment and storage until analysis. This is not mentioned on p4 lines27-29, so we assumed they were not frozen, in which case more should be made of the potential for change during storage than the one line given here, and the unfrozen time between collection and analysis should be stated.*

**Reply from authors**

Aerosol samples for single particle analysis are not kept in freezer to avoid morphology change and heterogeneous reactions by humidification. Some information and the unfrozen periods were added to “2.3 Aerosol sampling and measurements”.

***Comment from Referee***

*4. The description on p6 of Figures 3(a) to (e) bears little relation to the order of (a) to (e) in the Figure itself. Nor does the caption of Figure 3, which does not even mention Figure 3(e). This should be sorted out.*

**Reply from authors**

This point is our editorial error. We correct order of the pictures.

***Comment from Referee***

*5. From the scenario of frost flower formation given in the introduction, we would expect sulphate depletion in surface brine to be equal to that in the frost flowers - the flowers are expected to wick this brine, so if sulphate deposition occurs only in the colder temperatures above the surface then the frost flower total sample would contain the original brine sulphate. The fact of depletion in frost flowers but not brine in Figure 6 is a strange and new result, which deserves comment in p9 para1. Might it be related to the sampling protocol for surface brine given in p4 lines5-6? This suggests a large amount of solid was removed together with any liquid, thereby possibly incorporating ice into which sulphate had precipitated. This should be discussed, as it may also affect some of the discussion about changes in Mg, Br and Ca after 26 Feb.*

### Reply from authors

In our sampling, all body of frost flowers taken from sea-ice. On the other hands, brine, ice, and solid salts were samples ad “brine”, because it is difficult to segregate brine from slush (ice and solid salts). When some salts such as mirabilite and hydrohalite were precipitated in the slush layer, we cannot identify the evidence of salt precipitation from sea-salt ratios (e.g.,  $\text{SO}_4^{2-}/\text{Na}^+$ ). Temperature at surface of brine (base of frost flowers),  $T_{\text{FF}}$ , dropped to temperature at precipitation of mirabilite and hydrohalite, so that these salts might be precipitated and the n the residual brine might be migrated onto frost flowers. These description were added to “2.2 Sampling of frost flowers, brine, snow and sea-ice” and “4.2 Aging of frost flower and sea-salt fractionation”.

### Comment from Referee

*6. The discussion about possible removal of Br and I from frost flowers by heterogeneous reactions on 27 Feb (p10 lines21-21) stretch the apparent accuracy of the measurements - the difference between 0.00206 and 0.00214 for Br is surely not significant, given the scatter in Figure 4b. If the Br and I differences are significant, error bars should be derived.*

### Reply from authors

We agree with your comments. We added analytical error bars in determination in IC, IC-MS and ICP-MS into the plots of Fig. 6. Therefore,  $\text{Br}^-$  might be released slightly of insignificantly in our research conditions. On the other hands, iodine appeared to be released from frost flowers. Consequently, we updated description about  $\text{Br}^-/\text{Cl}^-$  and  $\text{I}/\text{Br}^-$  in frost flowers in the revised manuscript, as follows.

To elucidate halogen chemistry in frost flower, we compared between the features of  $\text{Br}^-/\text{Cl}^-$  and  $\text{I}/\text{Cl}^-$  in frost flowers at Site I. High correlation of  $\text{Cl}^-/\text{Na}^+$  and  $\text{Cl}^-$  enrichment strongly suggests that  $\text{Cl}^-$  release was insignificant from frost flowers and brine. Thus, we focus on the features of  $\text{Br}^-$  and I, here. we attempt to estimate the molar ratios of  $\text{Br}^-/\text{Cl}^-$  and  $\text{I}/\text{Cl}^-$  in frost flowers using the ratios of  $\text{Mg}^{2+}/\text{Cl}^-$ ,  $\text{Br}^-/\text{Cl}^-$  and  $\text{I}/\text{Cl}^-$  on 22–26 February, assuming that hydrohalite was not precipitated yet on 22–26 February, and that  $\text{Br}^-$  and I did not liberate from frost flowers through heterogeneous reactions. When the molar ratios on 22–26 February changed by the assumptions above, the molar ratios of  $\text{Br}^-/\text{Cl}^-$  and  $\text{I}/\text{Cl}^-$  in frost flowers after hydrohalite precipitation were estimated respectively as 0.00214 and  $1.82 \times 10^{-6}$ .

Although Br<sup>-</sup>/Cl<sup>-</sup> ratio (0.00206) was slightly lower than the estimated ratio, this difference might be very slightly or insignificant. Therefore, Br<sup>-</sup> release from frost flowers might be insignificant at Site I under the dusk conditions. On the other hands, the estimated I/Cl<sup>-</sup> ratio was higher than the ratios in frost flower ( $1.562 \times 10^{-6}$ ) on 27 February. The following likelihood should be considered: (1) reduction of I enrichment by precipitation of salts containing iodine, and (2) I release from frost flowers through heterogeneous reactions. Although NaBr•5H<sub>2</sub>O can be precipitated at -28 °C (Koop et al., 2000), no report in the relevant literature discusses a study of precipitation of iodine salts in sea salts. If iodine salts were not precipitated under the conditions at Site I, this difference implies the likelihood that I was released from frost flowers. Iodine can be released from frost flowers through the following heterogeneous reactions (Thompson and Zafiriou, 1983; Carpenter, 2003; Simpson et al., 2007; Saiz-Lopez et al., 2015).

***Comment from Referee***

*7. The statement on p17 line23 that sea salts (Mg etc) were “remarkably enriched” is not borne out by Figure 6. Depending on the error bars, they may not be enriched at all. If “remarkably” is removed, the sentence can probably stand, but better would be a derivation of error bars.*

**Reply from authors**

We addressed all of descriptions in “Concluding remarks”. Therefore, the sentences with “remarkably enriched” were removed from the revised manuscript.

***Comment from Referee***

*8. The caption to Figure 1 must contain some details of the broken lines described on p3. It is not acceptable to have figures with important features that are not described in the caption.*

**Reply from authors**

We added some details on the dash lines into the caption in Fig.1 Black, red, blue dash lines indicate locations of sea-ice breakage in November, 2013 and on 10-14 February, 2014, and 1 March, 2014, respectively.

All editorial comments were addressed in the revised manuscript.

## **Reply to Referee #2 (Dr. Dominé)**

We would like to thank your helpful comments to improve our manuscript. We responded to the general and specific comments. All comment are addressed in the revised manuscript. The updated sentences by your comments indicates blue words.

### ***Comment from Referee***

*The somewhat tedious point-by-point description of results should be completely replaced with a discussion focused on solving a few selected scientific questions such as for example: “how does the presence of FF affect aerosol composition?” or “what are the processes leading to halogen enrichment in FF and surface brine?”. More aggressive attempts to make deductions from the observations are mandatory.*

### **Reply from authors**

Thank you for your suggestions. We focused on sea-salt cycles in seasonal sea-ice area including sea-salt fractionation, aging processes of frost flowers, the fractionated sea-salt aerosols, and release processes of sea-salt aerosols from sea-ice surface on basis of our field evidences and previous works.

### ***Comment from Referee***

*The authors may cross their data with GOME2 BrO data to perhaps reach some interpretation on halogen activation.*

### **Reply from authors**

We agree with your suggestions. However, our measurement periods were too early to measure BrO and IO densities around northern areas of Greenland using satellite, because of lower solar angle. Thus, we did (could) not compare to BrO and IO data in the manuscript.

### ***Comment from Referee***

*1- Select a couple of novel scientific questions to be addressed by the data set. and 2- Select the data to be presented to address the selected questions. A couple of case studies focused on a few events may be interesting.*

### **Reply from authors**

As mentioned above, we focused on sea-salt cycles in seasonal sea-ice area including

sea-salt fractionation, aging processes of frost flowers, the fractionated sea-salt aerosols, and release processes of sea-salt aerosols from sea-ice surface on basis of our field evidences and previous works.

***Comment from Referee***

*3- Separate results and discussion and write in a much more concise form to produce a much shorter paper. ,*

*4- Reach some strong and novel conclusion. For example, finding out that the presence of FF does not significantly affect aerosol composition would be quite interesting. and*

*5- Place the data not used here but of potential interest to others in supplementary material or any other accessible place. The authors should feel free to adopt any other strategy, the objective being to make a good and concise use of the data to derive strong conclusions. At present, the manuscript is more a detailed preliminary campaign report than an actual scientific paper.*

**Reply from authors**

We separated Results and Discussion in the revised manuscript. Also we made an effort to concise form. Actually, we removed the description of sea-salt modification to “Supplementary” and remove some repetition of the statements and discussion. Additionally, we added our proposal (hypothesis) on sea-salt cycles in seasonal sea-ice area in “Concluding remarks”. Some data and descriptions (e.g., sea-salt concentrations in snow) were added into the section of Results and Discussion in the revised manuscript, because of comments from Referee#3.

***Comment from Referee***

*Vapor is supplied TO the atmosphere, not FROM. See the references on the same line. 2, 31. Specific surface areas are now expressed in  $m^2 kg^{-1}$ . Please convert.*

**Reply from authors**

These editorial points were addressed in the revised manuscript.

***Comment from Referee***

*Section 2.2. Was snow present in FF and brine samples? This should be mentioned as it dilutes the samples. Re. section 3.4.*

**Reply from authors**

Yes. During the campaign, snowfall and blowing snow occurred. On some frost flowers at Site I and II, snow was present slightly present to extent to that fine structure of frost flower was identified clearly. This statement was wadded to “2.2 Sampling of frost flowers, brine, snow, and seawater”.

***Comment from Referee***

*Please add a + sign: +1.8 °C, to avoid any ambiguity.*

*Throughout: replace liberated with released*

*Replace correlation with determination.*

**Reply from authors**

We added “+” sign in +1.8 °C. Words of “liberated” and “liberation” replaced to “released” and “release”, respectively in the revised manuscript.

***Comment from Referee***

*The structure of the paper is such that the mention of solar radiation here is a bit odd and unexpected, and maybe not readily understood by all. Separating results and discussion would have helped.*

**Reply from authors**

With modification of structure in the manuscript, results and discussion were separated in the revised manuscript, as already noted.

***Comment from Referee***

*A more in-depth discussion of the causes of Br and I enrichment is in order.*

**Reply from authors**

All description was moved to section of “4-1. Sea-salt fractionation on sea-ice”. Also, we added plausible processes for enrichment of Br<sup>-</sup> and I to the section. Then, we discussed each process, as follows.

Therefore, sea-salt fractionation by hydrohalite might be promoted in some samples of brine and frost flowers. Similar to Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Cl<sup>-</sup>, Br<sup>-</sup> and I can be enriched in frost flowers and brine by precipitation of mirabilite and hydrohalite. The plausible processes for enrichment of Br<sup>-</sup> and I can be listed as follows; (1) sea-salt fractionation

by precipitation of salts containing  $\text{Mg}^{2+}$  or  $\text{Cl}^-$  and (2) surface enrichment of  $\text{Br}^-$  and  $\text{I}^-$  in liquid phase (e.g., brine).  $\text{MgCl}_2$  and  $\text{MgSO}_4$  were identified in aerosol particles as shown in Figs. 8 and S3. Considering presence of  $\text{MgCl}_2$  and  $\text{MgSO}_4$  in aerosol particles, Mg salts might be localized or precipitated in frost flowers and slush layer. According to previous laboratory and model studies (e.g., Mairon et al., 1999),  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{KCl}$  (sylvite) can be precipitated approximately at  $-36^\circ\text{C}$  and  $-34^\circ\text{C}$ , respectively. During the measurements, minimum air temperature ( $-34.1^\circ\text{C}$ ) and temperature at surface of slush layer ( $T_{\text{FF}}$ ) were higher than temperature at  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  precipitation. Therefore,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  precipitation might not occur during the measurements, although precipitation of mirabilite and hydrohalite can occur. If strong vertical gradient of temperature near surface engender that temperature at brine surface or around top of frost flower dropped to temperature at precipitation of sylvite and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , these salts can be precipitated. However, temperature at brine surface or around top of frost flower might be higher than temperature for precipitation of sylvite and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  during the measurements. Thus, precipitation of sylvite and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  might not occur near surface of brine on sea-ice. Consequently, enrichment of  $\text{Br}^-$  and  $\text{I}^-$  in frost flowers might derive from sea-salt fractionation to a greater degree than precipitation of mirabilite and hydrohalite. In addition to sea-salt fractionation by precipitation of mirabilite, hydrohalite,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and sylvite, a molecular dynamics (MD) simulation conducted by Jungwirth and Tobias (2001) predicted considerable surface enhancement of  $\text{Br}^-$  and  $\text{I}^-$  in alkaline halide solutions. If  $\text{Br}^-$  and  $\text{I}^-$  prefer to be enhanced also at the brine surface, enrichment of  $\text{Br}^-$  and  $\text{I}^-$  might proceed in frost flower and brine by this surface enhancement and sea-salt fractionation.

These descriptions were added to “4-1. Sea-salt fractionation on sea-ice”.

***Comment from Referee***

*Air T is a useful variable for many purposes, but the actual variable of interest here is surface T. All the speculation between air T and processes is really not useful, unless a surface T can be produced. Several lengthy discussions could just be removed.*

**Reply from authors**

Although we showed air temperature measured by AWS ( $T_{\text{AWS}}$ ), our discussion was based on  $T_{\text{air}}$  (temperature above 10 cm from sea-ice surface) and  $T_{\text{FF}}$  (temperature at base of frost flowers) in the revised manuscript. We updated description in discussion

using air temperature in the sections of 4.1 and 4.2. Some sentences were removed from discussion in the revised manuscript.

***Comment from Referee***

*Replace larger by greater. The sea ice thickness may be important for the relationship between air and surface  $T$ , but not for surface processes.*

**Reply from authors**

We replaced “larger” to “greater” in the revised manuscript. Also, we rearrange the relation between  $T_{FF}$  and sea-ice thickness in “Concluding remarks”.

***Comment from Referee***

*10, 4-5. This statement does not lead to any useful conclusion. Please delete.*

**Reply from authors**

We removed this statement from the manuscript.

***Comment from Referee***

*Since or until ?*

**Reply from authors**

“Since” is correct.

***Comment from Referee***

*What useful conclusion do we derive from these Mg-rich and K-rich particles? Data description just is not enough for a scientific paper.*

**Reply from authors**

Presence of Mg-rich and K-rich sea-salt particles was direct evidence that the fractionated sea-salt particles were released from sea-ice area. We discussed more details about presence of these particles in the atmosphere, sea-salt fractionation, and release of the fractionated sea-salt particles to the atmosphere in the revised manuscript. The following discussion was added to “4-1. Sea-salt fractionation on sea-ice”.

Mg was enriched in sea-salt particles collected in this study. The following evidences

are important to discuss the origins of Mg-rich sea-salt particles and Mg-rich salt particles in the atmosphere: (1) presence of highly Mg-rich particles (Mg-rich sea-salts,  $\text{MgCl}_2$ , and  $\text{MgSO}_4$ ), (2)  $T_{\text{FF}}$  lower than temperature at precipitation of mirabilite and hydrohalite, (3) higher Mg/Na ratio in fine mode, and (4) small variability of Mg/Na ratio in strong winds and blowing snow. Because Mg-rich sea-salts and Mg-salts cannot be evaporated and vaporized under the ambient conditions, these particles must be released through physical processes. If sea-salt particles were fractured in the atmosphere, sea-salt fractionation can occur. However, direct evidence of fracture of sea-salt particles in the atmosphere has not been obtained (Lewis and Schwartz, 2004). With sea-salt fractionation in brine and frost flowers, sea-salt particles released from sea-ice had different sea-salt ratios from those of seawater, as discussed above. Actually,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  were enriched in frost flowers. Therefore, Mg-rich sea-salt particles (Fig.8b), K-rich sea-salt particles (Fig.8c), Mg-salt particles (Figs.8h-i), and K-salt particles (Fig.8j) might be originated from the sea-ice area and that they are associated with sea-salt fractionation.

***Comment from Referee***

*Could you please discuss the presence of non-sea salt sulphate?*

**Reply from authors**

Presence of nss-sulphate particles and some explanation were added to “3.7 Abundance of sea-salt particles and sea-salt-related particles”. Presence of nss-sulphates in sea-salt particles were already discussed in discussion of sea-salt modification, which we remove to Supplementary. Short discussion was added to “4-3. Fractionated sea-salt particles in the atmosphere”, because we focused on sea-salt cycles in the seasonal sea-ice areas in this study as follows.

Although the high aerosol number concentrations were observed occasionally at Siorapaluk under calm winds, the features might be caused by transport of (1) sea-salt particles released elsewhere by strong winds and (2) anthropogenic aerosols (i.e., sulphates and Arctic haze). Because of high abundance of sea-salt particles, most cases of higher aerosol number concentrations in calm winds were associated likely with release and transport of sea-salt particles. Similar phenomena were identified also in the Antarctic coasts (Hara et al., 2010).

***Comment from Referee***

*This is where your impressive data set could be put to good use to address these points. “At the moment, release processes of mirabilite-like and ikaite-like particles from the sea-ice surface without frost flowers remain unknown”. Sure, but is not this campaign supposed to contribute to solving this problem?*

### **Reply from authors**

We consider that presence of ikaite-like and mirabilite-like particles at Site III is an important evidence of sea-salt fractionation on sea-ice area and release of sea-salt particles from sea-ice. On basis of the evidence, we added more discussion about sea-salt fractionation near new sea-ice (Site III) to “4-3. Fractionated sea-salt particles in the atmosphere”, as follows.

Mg was enriched in sea-salt particles collected in this study. The following evidences are important to discuss the origins of Mg-rich sea-salt particles and Mg-rich salt particles in the atmosphere: (1) presence of highly Mg-rich particles (Mg-rich sea-salts,  $\text{MgCl}_2$ , and  $\text{MgSO}_4$ ), (2)  $T_{\text{FF}}$  lower than temperature at precipitation of mirabilite and hydrohalite, (3) higher Mg/Na ratio in fine mode, and (4) small variability of Mg/Na ratio in strong winds and blowing snow. Because Mg-rich sea-salts and Mg-salts cannot be evaporated and vaporized under the ambient conditions, these particles must be released through physical processes. If sea-salt particles were fractured in the atmosphere, sea-salt fractionation can occur. However, direct evidence of fracture of sea-salt particles in the atmosphere has not been obtained (Lewis and Schwartz, 2004). With sea-salt fractionation in brine and frost flowers, sea-salt particles released from sea-ice had different sea-salt ratios from those of seawater, as discussed above. Actually,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  were enriched in frost flowers. Therefore, Mg-rich sea-salt particles (Fig.8b), K-rich sea-salt particles (Fig.8c), Mg-salt particles (Figs.8h-i), and K-salt particles (Fig.8j) might be originated from the sea-ice area and that they are associated with sea-salt fractionation.

### **Comment from Referee**

*“Therefore, most of the aerosol particles around  $\text{Na}_2\text{SO}_4$  ratio in fine mode might be the modified sea-salt particles by heterogeneous reactions with  $\text{nss-SO}_4^{2-}$ .” Can’t you get to a stronger statement than just “might” by more in-depth examination of your data?*

*“Therefore, sea-salt modification (Cl loss) might be most likely to occur in fine mode.” Sure, you may even use your data quantitatively and examine the role of aerosol*

*surface to volume ratio on reaction kinetics. Again, “might” is not sufficient here.*

**Reply from authors**

We agree with your suggestions. We change “might” to “may” in the revised manuscript. Because we focused on sea-salt fractionation, description of sea-salt modification was moved to “Supplementary”. Role of aerosol surface area to volume ratio in sea-salt modification was already discussed in our previous studies (Hara et al., 2003, 2005, 2013). Thus, we mentioned this in Supplementary of the revised manuscript.

***Comment from Referee***

*Again, a more in-depth use of the data should allow useful conclusions, not vague suppositions.*

*These mentions of just observations, without any scientific deductions, are very disappointing.*

**Reply from authors**

Using our field evidences and results by previous works, we proposed sea-salt cycles in the seasonal sea-ice area in “Concluding remarks”. Because this proposal is hypothesis, this includes some speculation. We believe that our proposal (hypothesis) is useful and new set for sea-salt chemistry in the polar regions.

### **Reply to Referee #3**

We would like to thank your helpful comments to improve our manuscript. We responded to the general and specific comments. All comment are addressed in the revised manuscript. We separated Results and Discussion on basis of comment from Referee #2 (Dr. Dominé).

#### ***Comment from Referee***

*The manuscript lacks an error analysis that would allow one to determine the significance of results. Words like "significant" are used, but that is not clearly related to a rigorous statistical definition or simply a qualitative word. To make statements about composition being different from sea water ratios, the authors would need to discuss error analysis more rigorously.*

#### **Reply from authors**

Thank you for your helpful suggestion. We agree with your suggestion. We estimated analytical errors in each analytical method from reproducibility of determination of standard solutions with the concentrations with similar to the field samples. Error bars were added to Figures 4-6 and also plots in Supplementary. The description about the estimation of analytical errors was added to “2.4.1 Analysis of frost flower, brine, snow, and seawater”.

#### ***Comment from Referee***

*The manuscript contains many technical errors and is difficult to read due to nonstandard use of English.*

#### **Reply from authors**

We addressed editorial and technical errors in the revised manuscript. Our manuscript was checked by native English speaker (FASTEKJAPAN, URL <http://www.fastekjapan.com/greetings.htm>) before submission and revise.

#### ***Comment from Referee***

*The use of ternary plots is also not clear. Normally ternary plots are useful when the sum of the three components is 100%. However, in Figure 10, Cl, S, and Na are plotted as atomic percentages. These samples also have other atoms in their composition (e.g. oxygen that is a part of SO<sub>4</sub>, Mg, etc.), so I guess that the plots show atomic percentage*

*of Cl, S, and Na atoms?*

**Reply from authors**

As you pointed out, sum of atomic ratios of Na, S, and Mg (or Na, S, and Cl) was not 100 % in the most cases. Thus, we converted sum of the atomic ratios (e.g., Na-S-Mg) to 100% for ternary plot. This data conversion is common procedure for the ternary plot. These descriptions were added to “3.8 Sea-salt fractionation of aerosol particles in coarse and fine modes”.

***Comment from Referee***

*Some points are then very strange, such as on Figure 10b, three coarse points have >80% Cl and little Na. Something must charge balance the Cl-, but that is not clear on the plot.*

**Reply from authors**

This was already mentioned in description in sea-salt modification in the manuscript, as follows.

Some sea-salt particles had lower Na ratio and higher Cl ratio than the bulk seawater ratio. Mg was enriched considerably in the aerosol particles with lower Na ratios. Details of Mg enrichment are discussed ...

In the revised manuscript, the section about sea-salt modification was moved to Supplementary, because of suggestion by Referee #2 (Dr. Dominé).

***Comment from Referee***

*The paper often describes frost flowers as "fragile", while laboratory studies of frost flowers in a wind tunnel failed to produce aerosol, and field studies often show frost flowers get buried under blowing snow (e.g. snow blows while frost flowers remain intact). Therefore, there is not clarity in the literature that frost flowers are the only source of sea salt aerosol, and to the contrary, blowing snow and/or aerosol production from open water are often discussed in the literature. This manuscript doesn't describe the chemical composition of snow, which could be relevant to the production of aerosol, nor does it consider nearby open water and potential of aerosol production from that source.*

## Reply from authors

Thank you for your comments. We agree with you. We removed the word of “fragile” from the statements in the revised manuscript. In this study, we samples surface snow on sea-ice in this study, although surface snow was present patchily and snow sampling sites were several meters away from the sites of sampling of frost flowers and brine at Site I and II. Snow sampling procedures were added to “2.2 Sampling of frost flowers, brine, snow, and seawater”, as follows.

Snow on sea-ice was also taken using a clean stainless steel shovel from the location with snow accumulation (< 3 cm depth) without frost flowers at Site I, and II. Snow sampling was made approximately several –ten meters away from the site of sampling of frost flowers and brine. The pieces of frost flowers, brine (slush) , and snow samples, and snow were moved into each polyethylene bag (Whirl-pak; Nasco).

The data and description of surface snow were added to “3.3 Concentrations of sea salts in frost flowers, brine, and snow on sea ice” in the revised paper as follows.

By contrast, Na<sup>+</sup> concentration in snow samples collected on sea-ice was 1 – 2 orders lower than that of seawater. Na<sup>+</sup> concentration of fresh snow on sea-ice was lower than 0.1 mmol L<sup>-1</sup>. Na<sup>+</sup> concentration ranged in 0.4 – 3.2 mmol L<sup>-1</sup> in the aged snow on sea-ice.

Snow:

$$[\text{Cl}^-] = 1.315 [\text{Na}^+] + 0.02 \quad (R^2 = 0.972)$$

$$[\text{Mg}^{2+}] = 0.035 [\text{Na}^+] + 0.02 \quad (R^2 = 0.751)$$

$$[\text{K}^+] = 0.024 [\text{Na}^+] - 0.002 \quad (R^2 = 0.997)$$

$$[\text{Ca}^{2+}] = 0.026 [\text{Na}^+] + 2 \times 10^{-5} \quad (R^2 = 0.994)$$

In this study, we did not determine the concentrations of Br<sup>-</sup> and I<sup>-</sup> in the snow samples. (There are some descriptions)

Similar to the slopes of frost flower, slopes of K<sup>+</sup>-Na<sup>+</sup>, and Ca<sup>2+</sup>-Na<sup>+</sup> in snow on sea-ice were higher than seawater ratios. Slope of Mg<sup>2+</sup>-Na<sup>+</sup>, however, was lower than the seawater ratio, although fresh snow samples with the Na<sup>+</sup> concentration lower than 0.1 mmol L<sup>-1</sup> were distributed on the seawater ratios.

Also, we added discussion and explanation about release of sea-salt aerosols from sea-ice, snow, and open sea surface in discussion, as follows.

In “4-3. Fractionated sea-salt particles in the atmosphere”:

The atomic ratios of Na and S of the Mg-poor particles imply strongly that the particles were in the form of  $\text{Na}_2\text{SO}_4$ . If the sea-salt particles were modified with  $\text{SO}_4^{2-}$  by heterogeneous reactions, then the modified sea-salt particles contained sea-salt Mg. Thus, the presence of  $\text{Na}_2\text{SO}_4$  particles cannot be explained by their release from the sea surface.

Mg/Na ratios in sea-salt particles varied greatly depending on sampling site and meteorological conditions (e.g., winds and temperature) as shown in Fig. 11. Variations of Mg/Na ratios in sea-salt particles are very interesting to understand release processes of sea-salt particles from sea-ice surface. It should be noted that sea-salt particles at Site IIIa and IIIb were distributed around seawater ratios. Hence, sea-salt particles except mirabilite-like and ikaite-like particles at Site IIIa and IIIb might be released from sea surface, which were present off Site IIIa and IIIb on 2-3 March.

Additionally, we proposed sea-salt cycles in the seasonal sea ice areas from our field evidences and results by previous works. Schematic figure (Fig. 12) was added in the revised manuscript.

In “Concluding remarks”:

***First stage: seawater freezing***

Seawater starts freezing with decrease of air temperature. In this stage, sea-ice was present as conditions of grease-ice, frazil ice, and sludge. Considering that sea-salt particles with ratios similar to seawater were present only at Site IIIa and IIIb, these particles must be released from sea-surface in the initial stage and first stage. Depending on temperature at surface of sea-ice, ikaite starts precipitation, because temperature of ikaite precipitation is higher than that of mirabilite.

***Second stage: sea-ice formation and sea-salt fractionation***

Then, sea-surface was covered with thin sea-ice like Site IIIa and IIIb. Presence of sea-ice prevents release of sea-salt particles from sea surface to the atmosphere. Strong vertical gradient of air temperature near sea-ice surface resulted in frost flower formation. Some brine is migrated on frost flowers. Cooling of surface of frost flowers and brine can engender precipitation of ikaite and mirabilite. Ikaite-like and

mirabilite particles are released from frost flower and brine on sea-ice into the atmosphere. Ikaite-like particles and mirabilite-like particles are released into the atmosphere.

***Third stage: Frost flower growth and sea-salt fractionation***

With sea-ice growth, temperature on sea-ice ( $T_{FF}$ ) decrease gradually by reduction of heat conduction from seawater to sea-ice surface. Lower temperature on and in slush layer induce sea-salt fractionation by precipitation of mirabilite and hydrohalite. Sea-salt enrichment (e.g.,  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Br^-$  and iodine) proceed gradually in the residual brine by the Na-salt precipitation. The residual brine having Mg enrichment is migrated vertically on frost flowers. If air temperature at top of frost flowers decrease approximately to  $-33\text{ }^{\circ}C$  by the vertical gradient, sylvite and  $MgCl_2$  can be precipitated. Mg-rich sea-salt particles and Mg-salts are released from the brine and surface snow. Iodine is released into the atmosphere through heterogeneous reactions and  $Br^-$  were released slightly or insignificantly under the dusk conditions.

***Forth stage: Strong winds and snowfall on Frost flower***

Under the conditions with strong winds, snowfall and blowing snow, snow particles were attached on frost flowers and slush layer. As suggested by laboratory experiments (Roscoe et al., 2010), aerosol particles are released insignificantly from frost flowers. However, Mg-rich sea-salt particles and Mg-salts are released from the brine and surface snow by winds.

***Fifth stage: Frost flower covered with snow***

When snowfall and blowing snow are much enough to cover frost flowers and slush layer, frost flowers are buried completely in snow after the storm. Brine on sea-ice and frost flowers can be mixed into the snow layer. Sea-salt concentrations (salinity) in brine layer decrease gradually by migration and mixing into the snow layer. As a result, sea-ice surface (bottom of snow layer) freeze gradually. Sea-salts in the migrated brine and frost flowers can be redistributed through snow metamorphosis, although distributions of sea-salts might be heterogeneous in snow layer.

***Sixth stage: Snow erosion by strong winds***

Then, strong winds engender erosion of the snow layer. In other words, Mg-rich sea-salt particles are released into the atmosphere. Dry and hard surface of sea-ice appears after snow layer are removed completely.

### ***Comment from Referee***

*The manuscript claims in the abstract that "Aerosol number concentrations, particularly in coarse mode, were increased considerably by release from sea-ice surface under strong wind conditions." However, the figures and text really do not back up that claim. Figure 9 is presumably the data for this claim, but the authors do not indicate what periods to look at on that figure to see the effect they claim. In general, I see high coarse-mode aerosol on about DOY 12-18, 30, and 50-55. Those periods often have some winds, but not peak winds.*

### **Reply from authors**

During occurrence of blowing snow and strong winds, aerosol number concentrations increased by release of sea-salt aerosols from sea-ice area. As you pointed out, some high aerosol number concentrations without blowing snow and strong winds were identified on DOY 12-18, 30, 50-55. In the Arctic regions, high aerosol number concentrations are associated with (1) release of sea-salt particles by the strong winds and (2) transport of anthropogenic aerosols such as sulphates (i.e., Arctic haze). In our observations, the high aerosol number concentrations corresponded to (1) appearance of low clouds (fog) above open sea surface off Siorapaluk, (2) high abundance of sea-salt particles in both coarse and fine modes. Therefore, the high aerosol concentrations might be associated with sea-salt release from sea-ice and sea surface before transport to the sampling sites. Indeed, similar phenomena were observed at Syowa Station, Antarctica (Hara et al., JGR, 2010). These results and discussion were added to results and discussion.

In "3.7 Abundance of sea-salt particles and sea-salt-related particles":

Appearance of low clouds (fog) above open sea was added to Figure 9 using red + symbols.

High abundance of sea-salt particles corresponded to strong winds, high aerosol number concentrations, and appearance of low clouds (fog) above open sea off Siorapaluk.

In "4.3. Fractionated sea-salt particles in the atmosphere":

High aerosol number concentrations and high abundance of sea-salt particles with

Mg enrichment under strong winds implies that sea-salt particles were dispersed from sea-ice surface. Although the high aerosol number concentrations were observed occasionally at Siorapaluk under calm winds, the features might be caused by transport of (1) sea-salt particles released elsewhere by strong winds and (2) anthropogenic aerosols (i.e., sulphates and Arctic haze). Because of high abundance of sea-salt particles, most cases of higher aerosol number concentrations in calm winds were associated likely with release and transport of sea-salt particles. Similar phenomena were identified also in the Antarctic coasts (Hara et al., 2010).

#### ***Comment from Referee***

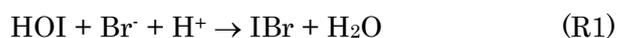
*The claim that bromide is being released from frost flowers made at the bottom of page 9 and page 10 would seem to imply a large release of bromine from frost flowers to the atmosphere. The authors should do a mass balance argument to indicate how much bromine would be released from this proposed release and compare the value to observations of atmospheric bromine (e.g. BrO). If that calculation led to unreasonably large BrO concentrations, then it would be evidence against this hypothesized direct halogen release. The lack of error analysis also makes it challenging to tell what is significant on these plots. Lastly, field evidence (Pratt et al., 2013) and multiple laboratory studies indicate that the pH of surfaces should be acidic for efficient halogen release, while highly saline samples were not efficient at releasing halogens.*

#### **Reply from authors**

On basis of your comments, we added the error bars to Figs. 4-6 and also plots in Supplementary in the revised manuscript. Considering analytical errors, Br<sup>-</sup> release from frost flowers might be slightly or insignificantly. Therefore, Br<sup>-</sup> release from frost flowers might be insignificant at Site I under the dusk conditions. On the other hands, the estimated I/Cl<sup>-</sup> ratio appeared to be released somewhat from frost flowers. From I/Cl<sup>-</sup> ratios, we estimated the released amount of iodine from frost flowers to ca. 16%. Therefore, we modified description about halogen release from frost flowers in “4-2. Aging of frost flower and sea-salt fractionation”, as follows.

To elucidate halogen chemistry in frost flower, we compared between the features of Br<sup>-</sup>/Cl<sup>-</sup> and I/Cl<sup>-</sup> in frost flowers at Site I. High correlation of Cl<sup>-</sup>·Na<sup>+</sup> and Cl<sup>-</sup> enrichment strongly suggests that Cl<sup>-</sup> release was insignificant from frost flowers and brine. Thus, we focus on the features of Br<sup>-</sup> and I, here. we attempt to estimate the

molar ratios of Br<sup>-</sup>/Cl<sup>-</sup> and I/Cl<sup>-</sup> in frost flowers using the ratios of Mg<sup>2+</sup>/Cl<sup>-</sup>, Br<sup>-</sup>/Cl<sup>-</sup> and I/Cl<sup>-</sup> on 22–26 February, assuming that hydrohalite was not precipitated yet on 22–26 February, and that Br<sup>-</sup> and I did not liberate from frost flowers through heterogeneous reactions. When the molar ratios on 22–26 February changed by the assumptions above, the molar ratios of Br<sup>-</sup>/Cl<sup>-</sup> and I/Cl<sup>-</sup> in frost flowers after hydrohalite precipitation were estimated respectively as 0.00214 and  $1.82 \times 10^{-6}$ . Although Br<sup>-</sup>/Cl<sup>-</sup> ratio (0.00206) was slightly lower than the estimated ratio, this difference might be very slightly or insignificant. Therefore, Br<sup>-</sup> release from frost flowers might be insignificant at Site I under the dusk conditions. On the other hands, the estimated I/Cl<sup>-</sup> ratio was higher than the ratios in frost flower ( $1.562 \times 10^{-6}$ ) on 27 February. The following likelihood should be considered: (1) reduction of I enrichment by precipitation of salts containing iodine, and (2) I release from frost flowers through heterogeneous reactions. Although NaBr•5H<sub>2</sub>O can be precipitated at -28 °C (Koop et al., 2000), no report in the relevant literature discusses a study of precipitation of iodine salts in sea salts. If iodine salts were not precipitated under the conditions at Site I, this difference implies the likelihood that I was released from frost flowers. Iodine can be released from frost flowers through the following heterogeneous reactions (Thompson and Zafiriou, 1983; Carpenter, 2003; Simpson et al., 2007; Saiz-Lopez et al., 2015).



Reactions of R4 can proceed under nighttime conditions. Other reactions, however, are enhanced under conditions with solar radiation because HOI can be formed efficiently through atmospheric photochemical reactions. Frost flowers at Site I had been exposed to direct solar radiation since 18 February, 2014, although it had been dusk at noon since early February. Therefore, the heterogeneous iodine loss from frost flowers can engender reduction of I enrichment after hydrohalite precipitation in frost flowers. From the I/Cl<sup>-</sup> ratios, amount of the released iodine from frost flowers can be estimated to ca. 16 % under our research conditions. The more solar radiation, the more reactive halogens might be released from frost flowers and brines. Comparing between the short-term features of Br<sup>-</sup>/Cl<sup>-</sup> and I/Cl<sup>-</sup> in frost flowers, heterogeneous I loss appears likely to occur from frost flowers relative to heterogeneous Br<sup>-</sup> loss.

### ***Comment from Referee***

*The referencing of the paper is not accurate. An example of this is on line 3-4 of page 3, which the authors say "Reportedly, Br<sup>-</sup> enrichment occurs in frost flowers at Barrow, Alaska (Douglas et al., 2012)...". However, the text of that citation says "There is no enhancement in bromide to chloride ratios in the frost flowers compared to brine or seawater".*

### **Reply from authors**

Douglas et al. (2012) estimated Br<sup>-</sup>/Cl<sup>-</sup> ratios in frost flowers and brine. Then, they evaluated Br<sup>-</sup> enrichment from the ratios. However, we calculated molar ratios of Br<sup>-</sup>/Na<sup>+</sup> from the data listed in Table 1 of Douglas et al. (2012). Br<sup>-</sup> appeared to be enriched relative to Na<sup>+</sup> slightly in some frost flower samples, although many frost flowers had insignificant Br<sup>-</sup>. Therefore, we addressed the statements in "Introduction", as follows.

Reportedly, Br<sup>-</sup> enrichment occurs slightly in frost flowers in the Weddell Sea, Antarctica (Rankin et al., 2002). Slight Br<sup>-</sup> enrichment to Na<sup>+</sup> was observed in a few samples collected at Barrow, Alaska, although there was no Br<sup>-</sup> enrichment in same samples of frost flowers and brine (Douglas et al., 2012). Additionally, results of some earlier studies have indicated non-significant Br<sup>-</sup> enrichment in frost flowers at Barrow and Hudson Bay (Alvarez-Aviles et al., 2008; Obbard et al., 2009).