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_4, 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 course 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^+ concentration in snow samples collected on sea-ice was $1 - 2$ orders lower than that of seawater. Na^+ concentration of fresh snow on sea-ice was lower than 0.1 mmol L^{-1}. Na^+ concentration ranged in $0.4 - 3.2$ mmol L^{-1} in the aged snow on sea-ice.

Snow:

$[Cl^-]$ = 1.315 $[Na^+]$ + 0.02 (R^2 =0.972)

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

$[K^+]$ = 0.024 $[Na^+]$ − 0.002 (R^2 =0.997)

$[Ca^{2+}]$ = 0.026 $[Na^+]$ + 2×10^{-5} (R^2 =0.994)

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

Similar to the slopes of frost flower, slopes of K^+-Na^+, and Ca^{2+}-Na^+ in snow on sea-ice were higher than seawater ratios. Slope of Mg^{2+}-Na^+, however, was lower than the seawater ratio, although fresh snow samples with the Na^+ concentration lower than 0.1 mmol L^{-1} 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 Na_2SO_4. If the sea-salt particles were modified with SO_4^{2-} by heterogeneous reactions, then the modified sea-salt particles contained sea-salt Mg. Thus, the presence of Na_2SO_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 °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.

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 they 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).
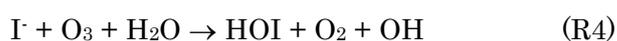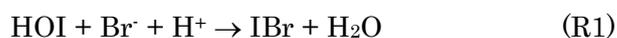
Comment from Referee

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^- release from frost flowers might be slightly or insignificantly. Therefore, Br^- release from frost flowers might be insignificant at Site I under the dusk conditions. On the other hands, the estimated I^-/Cl^- ratio appeared to be released somewhat from frost flowers. From I^-/Cl^- 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^-/Cl^- and I^-/Cl^- in frost flowers at Site I. High correlation of Cl^--Na^+ and Cl^- enrichment strongly suggests that Cl^- release was insignificant from frost flowers and brine. Thus, we focus on the features of Br^- and I^-, here. we attempt to estimate the

molar ratios of Br^-/Cl^- and I/Cl^- in frost flowers using the ratios of Mg^{2+}/Cl^-, Br^-/Cl^- and I/Cl^- on 22–26 February, assuming that hydrohalite was not precipitated yet on 22–26 February, and that 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 Br^-/Cl^- and I/Cl^- in frost flowers after hydrohalite precipitation were estimated respectively as 0.00214 and 1.82×10^{-6}. Although Br^-/Cl^- ratio (0.00206) was slightly lower than the estimated ratio, this difference might be very slightly or insignificant. Therefore, Br^- release from frost flowers might be insignificant at Site I under the dusk conditions. On the other hands, the estimated I/Cl^- ratio was higher than the ratios in frost flower (1.562×10^{-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 $NaBr \bullet 5H_2O$ 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).

$HOI + Br^- + H^+ \rightarrow IBr + H_2O$ (R1)

$I^- + H_2O_2 \rightarrow HOI + OH^-$ (R2)

$HOI + I^- + H^+ \rightarrow I_2 + H_2O$ (R3)

$I^- + O_3 + H_2O \rightarrow HOI + O_2 + OH$ (R4)

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^- 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^-/Cl^- and I/Cl^- in frost flowers, heterogeneous I loss appears likely to occur from frost flowers relative to heterogeneous Br^- loss.

Reply from authors

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

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