Reply to Referee #1 (Dr. Roscoe)

We would like to thank your helpful comments to improve our manuscript. All comments are responded and addressed in the current revise. The updated parts are indicated by red words in the revised manuscript (pdf file).

Comment from Referee: *Section 5 and Figure 11 present an excellent new speculative scientific conclusion, but there is no demonstration of how either relates to the discussion in Section 4. Also, the verbiage that is the revised Section 4 is so confused that it cannot yet be used to prove even elements of the scenario in Section 5 and Figure 11, let alone all of them.*

Reply from authors: We arranged descriptions in Section 4 (discussion) on basis of interpretation of "what the field measurements meant". In addition, we divide each process between shown and speculated from field evidences in Figure 12.

Details of our reply to each comment are as follows.

Comment from Referee: The discussions in the sub-sections of Section 4 are now hopelessly lengthy, tangled and confused. Section 4 needs a major rethink, and needs to be shortened.

Reply from authors: We shortened and rearranged the discussion section. In section 4, we attempted to focus on sea-salt fractionation on sea-ice and sea-salt cycles which can be shown statistically. Also, statistical analysis (t-test) was done in Section 3. Schematics about sea-salt cycles (Fig. 12) and descriptions moved from "conclusion" to Section 4 by suggestion from the referee #2.

Comment from Referee: *The points in Section 5 need to relate, in a very concise way, to the results of the discussion in Section 4. The authors admit that some of Section 5 is speculative, and this is no bad thing for such a comprehensive scenario, but Section 5 should identify (concisely, please) which elements are speculation, which follow from the work of others, and which follow from Section 4 and where in Section 4.*

Reply from authors: Schematics about sea-salt cycles (Fig. 12) were redrawn in Fig. 12

of the current revise. Highly speculated processes were removed from Fig. 12. Processes including some speculation were shown by dotted arrows with "?" marks, whereas processes shown from the field evidences were shown by thick arrows.

Comment from Referee: *The early part of Section 4.3 focuses on frost flowers as the source of particles. But the correlation between high particle density and strong winds, brought up later in Section 4.3, suggests that the earlier discussion in 4.3 is irrelevant. This earlier discussion should be discarded, or at least relegated to the end of the Section 4.3 and downplayed.*

Reply from authors: The description in early part of Section 4-3 was removed in the current revise.

Comment from Referee: Page 1 line 24 wrongly states that frost flowers are ice crystals that contain salts. In fact, they grow perfectly well on fresh-water ice. Perhaps the authors meant "In the sea-ice zone, frost flowers are usually ice crystals that contain salts ..." ?

Reply from authors: The sentence changed to "Frost flowers on sea-ice are ice crystals that contain brine and sea salts".

Comment from Referee: *Page 14 line 39 makes an incorrect claim about the frost-flower paper that I led in 2010. Our conclusion was that no particles were released from frost flowers, not that they were released non-significantly.*

Reply from authors: The statement was changed to "As suggested by laboratory experiments (Roscoe et al., 2010), no aerosol particles are released from frost flowers.".

Comment from Referee: *The material added in the revisions contains a large number of errors of grammar and syntax, even before Section 4. The revised sentences should be re-read carefully, and corrected - they have the hallmarks of being inserted in haste, and of not being read by all the co-authors.*

Reply from authors: We, all coauthors, checked the current revise. Additionally, the manuscript was checked by native English speaker (FASTEK, http://www.fastekjapan.com/). Our manuscript was written and checked in US English.

Reply to Referee #2

We would like to thank your helpful comments to improve our manuscript. All comments are responded and addressed in the current revise. The updated parts are indicated by red words in the revised manuscript (pdf file).

Comment from Referee: *While some effects are large (e.g. sulfate is depleted by a large factor (~5) compared to sea water ratios), many of them are small. Therefore, it is necessary to give a well described error analysis that accurately uses appropriate words. Error estimates are included, but for example in Figure 6, the error bars are not specified as 1-sigma or otherwise.*

Reply from authors: We used 1-sigma of reproducibility of determination in our analytical conditions as analytical errors in text and error bars in Figures. The descriptions were added to the text and figure captions. Furthermore, statements with strong wording (e.g., remarkably and markedly) were changed to “weaker wording”.

Comment from Referee: *The analyses of sea water (discussed further below) are not compared to literature values, and a quick comparison seems to show deviations of 10-20% from literature, which is on the order of potential analysis error, particularly when propagated into ratios.*

Reply from authors: As suggested by you (Referee #2), we compared seawater ratios in this study (seawater at Siorapaluk) and literatures (Lide, 2005; Millero et al., 2008; Millero, 2016). Although the molar ratios of seawater collected at Siorapaluk differed slightly in some species from the literature values (Lide, 2005; Millero et al., 2008; Millero, 2016), this difference was larger than analytical errors. Because seawater ratios were different at sampling sites (Millero, 2016), the difference might result from locality of seawater ratios. These statements were added into P.6 L. 11-19 in the current revise.

Comment from Referee: *For the weaker effects, a rigorous discussion of analytical errors is needed. A t-test could be used, but often errors are not truly normally distributed (they are non-Gaussian), so effects that are indicated to be "significant" in a statistical senses but are not far from the level of significance are not to be over interpreted.*

Reply from authors: We agree with your comment. T-test was applied for the molar ratios of frost flowers, brine, and snow. Results of t-test (t-values, p-values, and degree of freedom) were shown in Table 2 in the current revise. Description in Section 4 were rearranged on basis of the results of t-test. Therefore, large parts of discussion about Br- and I were removed from the text.

Comment from Referee: *The idea that blowing snow may be a source of sea salt aerosol is still not truly considered in this manuscript. Instead the authors stay with the idea of the prior manuscript that sea salt aerosol essentially come from frost flowers. The manuscript appears to show photographic evidence for blowing snow. Figure 3, panel f shows the "condition of old sea ice on 2 March, immediately after the storm", which is clearly scoured of snow. Photographs on earlier days (Figure 3, panels (a), (c), and (d)) clearly show snow on the sea ice. Apparently this snow was blown away, and as snow blows, it sublimes, producing aerosol particles. Open sea water can also lead to production of sea salt aerosol.*

Reply from authors: As shown in Fig. 12, we proposed sea-salt emission by blowing snow. At Sites I and II with slush layer, snow layer was not blown away completely in contrast to surface condition on old and very-old sea-ice after storm conditions. Because slush layer and surface snow on new and young sea-ice were wet, snow erosion might be less efficient on new and young sea-ice with slush layer than on old and very-old sea-ice. Of course, sea-salt particles can be released from surface snow on new and young sea-ice through snow erosion. This difference is likely important to elucidate sea-salt cycles on seasonal sea-ice areas. Some descriptions about sea-ice/snow conditions were added into Sections of 3.2, 4.3, and 4.4 in the current revise. Emission of sea-salt particles from open sea water was identified dominantly at Sites IIIa and IIIb in this study. The statements were shown in Sections of 4.3 and 4.4.

Comment from Referee: *Figure (12), has some good ideas in it, but does not belong in the conclusions (it is a discussion point and some of the text related to it are not reasonable conclusions of the present study). Some aspects of this discussion that are taken too far by the authors include the following. In the "Initial stage", bubble bursting releases particles from the surface microlayer of the ocean. This microlayer is organic-rich, and could potentially include inorganic counter ions selected by the organic species. In the second stage, it is posited that "ikaite-like and mirability particles are released from frost flowers and brine on sea ice into the atmosphere". What physical release mechanism is being proposed here? For the frost flowers to be depleted in sulfate with respect to chloride, there must be a physical separation of brine (depleted in sulfate) from* *mirabalite crystals. The normally discussed mechanism is that the mirabilite is left in the brine on the sea ice, and the sulfate-depleted brine migrates up the frost flower. That would leave the mirabilite further from the atmosphere and seems to not be compatible with production of mirabilite particles in the atmosphere. The text needs to posit a mechanism for this effect, and it should be discussed, as the results of the manuscript don't appear to prove such a mechanism exists. The "third stage" indicates that it is concluded that "iodine is released into the atmosphere through heterogeneous reactions and* Br^- *is released slightly or non-significantly under dusk conditions. The more solar radiation, the more reactive halogens can be released from frost flowers and brines." This statement is way too far for the results shown. Remember that the results show slight enhancements in* Br^- *and* I^- *in the older frost flowers. The argument for* I^- *release is that* I^- *is less enhanced than* Br^-*, but again these enhancements are small and analytically suspect in themselves, their differences are even smaller. Lastly, how can the study that says bromide is not released conclude that with more solar radiation there is release of bromide? In the fourth stage, the lack of release of particles by wind from frost flowers is discussed to somehow conclude that Mg-enriched particles are released by wind?*

Reply from authors: As suggested from you (referee #2), Fig. 12 and the statements moved from “Concluding remarks” to Section 4.4 (discussion).
In your comment on “Initial stage”, microlayer and organics were pointed out. It is true that presence of microlayer and organics have some potentials to modify constituents of sea-salt particles released from sea surface, but Keene et al. (2010) showed sea-salt ratios in particles released from bubble bursting were similar to the seawater ratios. Because we did not analyze and discuss organics in this study, description about microlayer and organics was not added in the revised manuscript. Instead, early work by Keene et al. (2010) was cited in the text.
In Second stage, ikaite-like and mirabilite-like particles were present at Sites IIIa and IIIb. Because these particles cannot be vaporized in ambient conditions, these particles must be released through physical processes. Considering these particles were identified only at IIIa and IIIb, these particles might be released from fresh and new sea-ice area. As shown in our results and pointed by you, mirabilite might be precipitated on sea-ice and brine. Then the residual brine (i.e., sulfate-depleted brine) can be migrated onto frost flower at Sites I and II. However, SO_4^{2-}/Na^+ ratios at Sites IIIa and IIIb were higher than those at Sites I and II. This difference indicated that less-sulfate-depleted brine were migrated onto frost flowers at Sites IIIa and IIIb. Therefore, mirabilite might be distributed on both brine and frost flowers at new sea-ice area. However, specific release

processes of ikaite-like and mirabilite-like particles were still unknown. These statements were added to Sections 4.3 and 4.4.

Third stage: The molar ratios of Br^-/Cl^- and I/Cl^- in frost flower were mostly higher than those in brines, except for a few brine samples. It is expected that Br^- and I were richer in frost flowers because of sea-salt fractionation. However, the differences of change of Br^-/Cl^- and I/Cl^- were not significant in t-test. Therefore, statements about likelihood of release of Br^- and I were excluded in the current revise.

Fourth stage: Similar to ikaite-like and mirabilite-like particles, Mg-rich sea-salt particles and Mg-salt particles must be released though physical processes from frost flowers, brine, and snow. Considering the direct evidence of Mg depletion in aged surface snow on sea-ice, Mg-rich sea-salt particles and Mg-salt particles were likely released from surface snow mixed with the residual brine on sea-ice. The variations of Mg/Na ratios in sea-salt particles were smaller in both coarse and fine modes under storm conditions (DOY = 40 and 59), although the Mg/Na ratios were higher than the seawater ratio. Winds passed from the old and very-old sea-ice area to the sampling sites in the storm conditions. Consequently, Mg-rich sea-salt particles in the storms might be released also from the snow layer on old and very-old sea ice through erosion of snow by strong winds because the slush layer was absent on old and very-old sea ice. By contrast, Mg/Na ratios were varied largely under calm wind conditions. To explain the presence of highly Mg-rich sea-salt particles and Mg-rich salt particles, we inferred that these particles were released from the aged surface snow and the residual brine on slush layer and frost flowers through erosion of snow with the residual brine and splashing and shattering of the residual brine film. Higher Mg/Na ratios in fine sea-salt particles are eminently explainable if the processes proceeded on seasonal sea-ice areas. These statements were added to Sections 4.3 and 4.4.

Comment from Referee: *The text has been modified, but the abstract has been modified very little. Line 18 of page 1 discussed heterogeneous SO_4^{2-} formation that is not really discussed in the text anymore.*

Reply from authors: Although sea-salt modification was shown in supplementary information, the statement in abstract was changed to “Sulfate depletion by sea-salt fractionation was found to be slight in sea-salt aerosols because of the presence of non-sea-salt SO_4^{2-}”.

Comment from Referee: *Page 2, line 13: This says that sea salt is an ice nucleus (IN),* *which seems surprising given that most IN are not soluble. Give a reference or cut this text. page 2, line 23: Again it is said that salt is an IN.*

Reply from authors: Some recent studies pointed out that sea-salts have potential to ice nuclei. Some references were added in the text.

Comment from Referee: *page 2, lines 32-38: This section is about fractionation in a section nominally about "modification". Move to the other section about fractionation. A clearer description of how "fractionation" differs from "modification" would also be useful.*

Reply from authors: We agree with your comment. These descriptions moved to section on "sea-salt fractionation". In this study, sea-salt fractionation and modification indicate, respectively, change of molar ratios in sea-salts through salt precipitation and heterogeneous reactions. The mention was shown in P.2 L1-2 and L31-32.

Comment from Referee: page 3, section 2.1: Give a clearer definition of new, young, old, very old ice.

Reply from authors: New, young, old, and very old sea-ice were defined by sea-ice age in this study. Some description was added in P.3 L. 12-18.

Comment from Referee: page 5, line 7: There is a shift here from mass based concentrations to molar based ratios. Make that shift more clear in the text.

Reply from authors: For more clear mention, we show "molar concentration" in the text (p.5 L.11).

Comment from Referee: *The slopes of the correlations are unitless, but the intercept has the unit of the concentration, and thus is important. This intercept is often trivially small, but for two cases, the intercept may have an effect, specifically the Mg2+ correlation to Na+ in snow shows a very different slope than the other species, but also an intercept that is similar to actual snow Mg2+ snow concentrations. The brine Cl- to Na+ comparison may also be affected by this offset. It also needs to be noted that ion ratios (calculated in other places) are equivalent to slopes of correlation plots only when the intercept is zero. When the intercept is non-zero, the slope of a correlation plot will differ from the ratio of the ion concentrations. On page 6, line 40, the authors indicate* *that ratios to Na+ are consistent with sea salt fractionation (by mirabalite precipitation), which they are, but these changes are relatively small because there is much more Na+ than SO4-- in sea water, so sulfate limits the removal of Na+. Therefore, what should be pointed out is that SO2-- is depleted compared to either Na+ or Cl-, which is clearer evidence of mirabilite precipitation. The magnitude of these changes appear consistent.*

Reply from authors: We agree with your comments. As pointed out from you, the slopes in the relations might be close to the ambient molar ratios, when the intercepts are close to zero. The slopes of the relations can be biased positively in cases of contamination/mixing of non-sea-salt species such as minerals and anthropogenic species, which can be deposited onto surfaces of frost flowers, brines, and snows. In contrast, the ratios can be biased negatively in cases of sea-salt fractionation on sea-ice and depletion/release of the continents in frost flowers, brines, and snows into the atmosphere. The molar ratios in frost flowers, brines, and snow are presented in Table 1. With the exception of Mg^{2+}/Na^{+} in snow and I/Na^{+} in frost flowers and brine, the molar ratios conform to the slopes. The intercept values and the coefficients of determination in these ratios are, respectively, larger and smaller than the other ratios. These descriptions were added to Section 3.3 (p.7 L.8-15). Also, explanation about mirabilite precipitation was added in Section 3.3 (p. 7, L.17-37).

Comment from Referee: *The treatment of sea water ratios and their errors is still lacking in this discussion. Specifically, Table 1 shows the ratio of Br- to Na+ and Cl- from literature (Lide, 2005). However, the analyses of sea water are used for the other ratios. When I look up sea water ratios to Na+, I find the following values, which are then compared to the analysis results from seawater (n=2) in Table 1, which is in parentheses following the literature values: K+/Na+ = 0.022 (0.020), Mg2+/Na+ = 0.113 (0.091), Ca2+/Na+ = 0.022 (0.020), Cl-/Na+ = 1.164 (1.227), and SO4--/Na+ = 0.060 (0.0613). These differences are on the order of 10-20%. They could be true differences between the sea water sampled as compared to standard sea water, or they could be small analytical errors. However, it is important that the present study used only a literature value for the Br-/Cl- ratio and then compares to analytical results to say that Br-/Cl- ratio is larger in frost flowers than in sea water. The magnitude of the enrichment is ~20%, which is comparable to the differences between the sampled sea water and literature sea water. Therefore, it is not clear to me that the "result" of bromide enrichment is a true result. Given the magnitude of errors, this result should be a minor one rather than a serious highlight of the results.*

Reply from authors: We compare sea-salt ratios in seawater at Siorapaluk to the literature values (Lide, 2005, Millero et al., 2008; Millero, 2016). As mentioned in above comment, sea-salt ratios differed even in respective literatures (Lide, 2005, Millero et al., 2008; Millero, 2016) because of locality shown by Millero (2016). Details were mentioned in P.6 L.11-19 in current revise. Because of the differences, we used seawater ratios at Siorapaluk in this study, although literature values were used for seawater ratios of Br^- and I.

Comment from Referee: *This discussion is interesting and clearly reiterates the point of sulfate being depleted in frost flowers but not in brine. The effects on other ions are relatively small, but the wording of the discussion does not reflect the small magnitude of these changes and still lacks a complete error discussion. For example, page 7 line 32 indicates that Mg2+/Cl-, K+/Cl-, and Ca2+/Cl- "increased remarkably". These increases are on the order of 10-20%, and not too different from reported error bar magnitudes. The wording needs to be more reflective of the actual magnitude of the effect. Additionally, the errors are indicated as "analytical errors" in the caption of Figure 6, but that is not a clear indication of the type of error. If these are 1-sigma error bars, that should be noted. The results section does not point out the large difference (factor of 5) present in sulfate ratios, but instead focuses on small changes that appear near error estimates. Additionally, in the start of this section (lines 17-18 of page 7), the text should more clearly make a correspondence between the terms "aged, young, fresh" frost flowers and the sampling sites.*

Reply from authors: As mentioned above, analytical errors and error bars mean 1-sigma values of reproducibility of determination. The mention was added into the text and figure captions. To elucidate the sea-salt ratios changed by precipitation of mirabilite and hydrohalite, we estimated the sea-salt ratios in frost flowers, although ratios of Mg^{2+}/Cl^-, K^+/Cl^-, and Ca^{2+}/Cl^- do not change by mirabilite precipitation. Procedures and assumption were added into Sections 3.3 (P. 7 L.24-37) and 3.4 (P.9 L.7 – p.10 L.5).

Comment from Referee: *The observation of Mg2+ enhancement in aerosol particles is an interesting one. Figure 11 should include a sea water ratio line (0.113 from literature, but 0.091 from sea water analysis in this work). Given that Figure 11 shows no wind speed, it is very challenging to confirm the statement "In conditions of blowing or drifting snow and strong winds, the Mg/Na ratios and the standard deviations decreased in both* *modes...". This needs to be more clearly presented. The storm of 1 March is noted, but the figure shows day of year. The text should indicate the DOY of this storm.*

Reply from authors: Lines of seawater ratios and plot of wind speed were added into Fig. 11. Short explanations were added to the text in Section 3.9 (p.12 L.4-11). DOY of 1 March was also indicated in the text.

Comment from Referee: *This section indicates that Mg/Na ratios decreased (towards sea salt ratios) during blowing snow and strong winds. However, page 13, line 20 indicates that Mg is enriched during strong winds. These two statements appear to conflict.*

Reply from authors: The description in Section 3.9 was modified to avoid confusion and miss-understanding of readers, as follows. In conditions with blowing snow or strong winds (>5 m s^{-1}), the Mg/Na ratios and their standard deviation tended to decrease in both modes (particularly in fine mode). For instance, median Mg/Na ratios in strong winds were ca. 0.18 in both modes on DOY = 40 (10 February), and ca. 0.16 in coarse mode and 0.22 in fine mode on DOY = 59 (1 March).

Comment from Referee: *page 10, lines 12-36 are mostly speculation, and their only basis is results that are probably close to analytical error limits.*

Reply from authors: The ratios of Br^-/Cl^- and I/Cl^- in frost flowers were mostly higher than those in brines, except for a few brine samples. It is expected that Br^- and I were richer in frost flowers because of sea-salt fractionation. However, t-test indicated that the difference between frost flowers and brines was insignificant. Most of discussion about enrichment of Br^- and I were removed in the current revise, although short statement was shown in the text in Section 4.4 (P.12 L.28-37). In Section 4.1, we focused on occurrence of sea-salt fractionation by mirabilite precipitation on basis of the results of t-test.

Comment from Referee: *page 11, line 11 overstates the "drastic change". Also, lower in this section, lines 23 and 24 indicate significant and non-significant changes that seem similar to the eye and have no statistical basis.*

Reply from authors: To elucidate change of molar ratios by precipitation of mirabilite and hydrohalite, we estimated the sea-salts. Simultaneous change of the ratios of

Mg^{2+}/Cl^-, K^+/Cl^-, Ca^{2+}/Cl^-, Na^+/Cl^-, Br^-/Cl^-, and I/Cl^- implies that hydrohalite precipitation proceeded at Site I. Indeed, difference of the ratios between 24-27 February and 26-28 February was 2-3 times greater than analytical errors. Therefore, the differences might be attributed to sea-salt fractionation (hydrohalite precipitation). Discussion was modified in the text of P.13 L.16-30.

Comment from Referee: *page 11, line 36: I have no clue how these molar ratios were generated; please explain more, or more likely cut this section.*

Reply from authors: As mentioned in above comments, the procedures of the estimation were added to the statements in Sections 3.3 and 3.4.

Comment from Referee: *page 11, line 42: A tiny difference is being used to justify a broad statement of "likelihood that I was released". This is really wild speculation. Iodide is not even a conserved species in sea water, so drawing this line is not straightforward from the literature. This wild speculation continues through page 12, line 16.*

Reply from authors: This statement about I release were excluded from discussion because ambient I/Cl^- ratios of seawater at Siorapaluk were uncertain in this study.

Comment from Referee: page 13, line 20: This statement conflicts with page 9, section 3.9.

Reply from authors: This comment was responded in above comment.

Comment from Referee: *page 14, lines 1-6 are truly conclusions from this work. Other true conclusions should be added to this section to make a new conclusions section. The reminder of the new "conclusions" should be moved to a discussion, as these points are really a discussion of potential ideas about sea salt aerosol formation related to sea ice. As discussed earlier, this discussion should be narrowed to what is defensible from the observations in this manuscript and/or points already in the literature (with citation of those literature sources). The current discussion lacks appropriate citation.*

Reply from authors: As suggested from you (referee #2), Fig. 12 and the statements moved from concluding remarks to Section 4.4 (discussion). Also citations were also added in each site of the text in Section 4.4. More conclusions were added into

“Concluding remarks”.