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., SO_4^{2-}/Na^+). Temperature at surface of brine (base of frost flowers), T_{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, 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 Br^-/Cl^- and I/Br^- in frost flowers in the revised manuscript, 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).

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.