Reply to Referee #1

We would like to thank useful comments for improvement of our manuscript. Statements were corrected on the basis of referee's comments as follows.

Referee's comment: In general large parts of the Results and Discussion section could be written more concisely. There are several repetitions, especially concerning chapters 3.4, 3.5 and 3.6, making the text somewhat exhausting and a challenge for the readers' endurance.

Reply from Authors: We attempt to arrange the statements in sections of 3.4-3.6. Several repetitions were removed from the text.

Referee's comment: Furthermore, potential consequences of single particle modification and fractionation after sampling (storage as well as high vacuum conditions under SEM-EDX analysis) should be discussed or an adequate reference should be provided.

Reply from Authors: We added some references in the text as follows;

After direct sampling, aerosol samples were kept in air tight boxes including desiccant until analysis in our laboratory in Japan to avoid humidification that can engender morphological change, modification (chemical reactions), and fractionation, as described by Hara et al. (2002, 2005, 2013). Therefore, aerosol modification and fractionation might be negligible, although aerosol constituents can be localized in each aerosol particle because of deliquescence of deliquescent aerosol particles under dry conditions.

Referee's comment: Chapter 2-3-1, Page 11398, lines 21-22: Please clarify: Is 23-25 s the temporal resolution of the measurement? How long was the typical over-all sampling period at each site?

Reply from Authors: Yes. Time of 23-25 s is measuring resolution. Aerosol number concentrations were measured during direct aerosol sampling at camp sites. Because sampling time was shown in Section of 2-3-2, we modified the description here as follows;

Aerosol number concentrations were recorded in resolution of every 23–25 s (corresponding to 1 liter air sucking) during direct aerosol sampling.

Referee's comment: Chapter 2-3-2, Page 11399, lines 18-22: Did you analyze all sampled particles? If not, please specify the percentage/fraction of the analyzed fine and coarse mode particles.

Reply from Authors:
Because of low number density on the sampling substrates in coarse mode, most aerosol-sampled area on the substrates was analyzed in this study. In some samples, we analyzed all coarse particles on the substrates. On the other hand, 20 – 30 % of aerosol-sampled area on the substrates was analyzed in aerosol samples in fine mode.

The description is modified in the text as follows;

In aerosol samples in coarse mode, most aerosol-sampled area on the substrates was analyzed in this study. Although we attempted to analyze as many coarse particles as possible, the lower aerosol number concentrations in coarse mode limit the number of the analyzed aerosol particles in this study. On the other hand, 20 – 30 % of aerosol-sampled area on the substrates was analyzed in aerosol samples in fine mode.

Referee's comment: Page 11400, lines 19-20: What is the meaning of ": : :the diurnal maxima were mutually
synchronized: : :"?

Reply from Authors:
Features of wind speed was synchronized to those of air temperature. The description is modified in the text as follows;

However, the diurnal maxima of wind speed were mutually synchronized well to those of air temperature at latitudes higher than 74 °S, when their diurnal features occur.

Referee's comment: Chapter 3-1-2, Page 11401: Please specify the method of trajectory calculation (isentropic, 3-dimensional, : : :) and provide a description of the colour code for Fig. 3 (what is meant with "latitude"? Is it the starting point of the respective trajectory?).

Reply from Authors:
Methods of trajectory calculation were described already in the text as follows;

“the 5-day backward trajectory was computed using the NCEP reanalysis dataset and kinematic mode in this study (Draxler and Rolph, 2013).”

Because words of “vertical motion mode” were used in HYSPLIT web page, the description in text was modified to

“the 5-day backward trajectory was computed using the NCEP reanalysis dataset and vertical motion mode in this study (Draxler and Rolph, 2013).”

Color code in Fig.3 indicates latitude at starting points of trajectory. The following explanation was added into caption in Fig.3.

Color code corresponds to latitude at starting points of trajectory.

Referee’s comment: It should also be noted that especially the reliability of vertical (but also lateral) movement of a given trajectory may be very low due to the lack of appropriate meteorological data from continental Antarctica. This has to be considered when interpreting the data.

Reply from Authors: The following description about reliability (uncertainty) of trajectory analysis was added into the text in the revised manuscript.

Uncertainty of trajectory analysis is derived from resolution of meteorological data (wind field), calculation scheme, and trajectory model. Kahl et al. (1989) and Stohl et al. (1995) presented that error reached to ~1000 km after trajectory calculation for 5 days. Therefore, the 5-day backward trajectory was analyzed in this study. Indeed, previous works (Reijmer et al., 2001, 2002; Hara et al., 2004, 2013; Suzuki et al., 2008) used 5-day backward trajectory analysis to discuss origins of moisture and aerosols. In general, uncertainty can be larger when starting altitude of trajectories is located in boundary layer. The 5-day backward trajectories from altitudes in boundary layer – free troposphere, however, were consistent well with vertical profiles of aerosol constituents over Syowa Station, Antarctica (Hara et al., 2013). In this study, we calculated the trajectories from 200, 500, and 1000 m above ground level. The trajectories showed similar vertical features and transport pathway in most cases, so that 5-day backward trajectory might be applied to discuss air mass history even in the Antarctic continent.

Referee's comment: Chapter 3-3, Page 11405, lines 6-8: Did you consider the "satellites" in your analyses?

Reply from Authors: Yes. But most signals may be derived from center nuclei of the "satellite".

Referee's comment: Chapter 3-3, Page 11405, lines 13-14: Please specify the term "stain or staining"!

Reply from Authors: "Stain" is correct. We changed to "stain" in the text.

Referee's comment: In addition, the particles presented in Fig. 6 are in both cases clearly smaller than 2 micrometer, but 6b (upper picture?) was denoted by coarse mode particle. Was there some kind of shrinking process during SEM analysis under high vacuum conditions?

Reply from Authors: We use "aerodynamic diameter" in the cut-off diameter. Aerodynamic diameter was estimated in particles density of 1 g cm^{-3}. Density of aerosol particles is larger, for instance, NaCl (2.2 g cm^{-3}), and H_2SO_4 (1.84 g cm^{-3}). Therefore, aerosol particles slightly smaller than the cut-off diameter can be collected on the sample substrates, depending on particle density.

These explanations were added into the text in Section 2-3-2.

Furthermore, most aerosol particles in atmosphere contain water in this study. The stain around particles was direct evidence of presence of liquid phase. After sampling, aerosol samples were kept under dry conditions. Aerosol particles were exposed in high vacuum condition in SEM-EDX analysis. Thus, dry and high vacuum conditions can cause water evaporation from aerosol particles. Therefore, small residual of water soluble and insoluble matters remained inside of the stain or satellite structure on the substrates, as shown in Fig.6.

Referee's comment: Chapter 3-4, Page 11405-11406: Being no expert in EDX analysis like probably most of the potential readers, some words about the reliability of this method would be helpful, especially in terms of the specific problem, that for large coarse mode particles potentially mainly the surface composition is probed, which may not be representative for the whole particle.

Reply from Authors: Analytical depth in SEM-EDX analysis depends on accelerating voltage, chemical compositions, density, and others. Although secondary electron can be emitted from depth of ~10 nm (e.g., Ding et al., 2009), characteristic X-ray can be emitted from depth of a few micrometer (e.g., Goldstein *et al*. 2003). Most of coarse particles were smaller than 3 micrometer in diameter in this study. Thus, characteristic X-rays were obtained from whole particle in fine and coarse mode in this study. When thickness of particles is larger than ca. 5 micrometer, compositions near surface (thickness of a few micrometer) may be detected. However, only a few particles larger than 5 micrometer were present in one sample.

These descriptions were added into the text.

Referee's comment: Page 11410, lines 4-6: The conclusion that differences of the relative abundance between incoming and outgoing traverse were caused by seasonal features appears arguable. I suggest that different general weather situation and meteorological effects could have played a significant role.

Reply from Authors: Although blizzard by cyclone approach occurs until early December at Syowa Station, few blizzards occur in mid-December – January (Sato and Hirasawa, 2007). The seasonal feature of cyclone approach relate closely to origins of air masses over the Antarctic continent as suggested by Suzuki et al. (2013). Therefore, the difference of the relative abundance between in the incoming traverse and in the outgoing traverse might correspond to seasonal features of sea-salt particles, air mass origins, and transport pathway from the end of spring toward summer on the Antarctic continent.

The descriptions in the text were changed to above sentences.

Referee's comment: Pages 11411-11413, lines 14-15, 3-4, 19-21, and 5-8: Please specify the corresponding detection limits.

Reply from Authors: Mean analyzed particles in each sample were 58 particles in coarse modes and 963 particles in fine mode. Detection limit of relative abundance was ca. 0.1 % in fine mode and 1-2 % in coarse mode except the samples with lower aerosol density on the substrate in coarse mode.

These descriptions were added into the text.

Referee's comment: Page 11411, lines 9-10: ": : : Figure 5 shows [: : :] lower near the surface on the Antarctic continent" – for me it is not obvious that Figure 5 really shows this! Please clarify.

Reply from Authors: The description about Figure 5 seemed to give you confusion, and was necessary for what authors want to discuss. Therefore, the description was removed from the text.

Referee's comment: Page 11411, lines 11-13: ": : : sulphate particles can be grown to coarse mode through coagulation and condensation: : :" – To me this sounds rather unrealistic! Most probably sulphate in super-micron aerosol has been formed by heterogeneous chemical processes on the surface of pre-existing coarse mode sea salt or mineral dust particles or by cloud processes (see chapter 3.5.3).

Reply from Authors: Coarse sulfate particles did not contain Na, Al, or Si, so that these particles might be composed of SO_4^{2-} and $CH_3SO_3^-$, as suggested previous works by Hara et al., 1995. Therefore, coarse sulfate particles can be grown to coarse mode through (1) hygroscopic growth, (2) cloud processes, (3) heterogeneous sulfate formation and (4) coagulation and condensation of condensable vapors (e.g., H_2SO_4 gas) under conditions with the low number concentrations of pre-existing particles on the Antarctic continent.

The sentences were added into the text.

Referee's comment: Page 11411, lines 19-21: Here again: seasonal features causing the differences in K-rich particles appear arguable.

Reply from Authors: Similar to discussion about features of sea-salt particles, this difference implies seasonal features of K-rich sulfate particles, air mass origins, and transport pathway in the inland area during late-spring – summer.

The descriptions in the text were changed to above sentences.

Referee's comment: Page 11416, lines 6-11: I do not really understand why high Cl/Na ratios (and strong winds) indicate surface generated sea-salt particles modified by HNO3 (I would suppose low Cl/Na ratios in this case).

Reply from Authors: We attempt modify sentences easy to explain as follows,

As discussed in sections of 3-2 and 3-5-1, therefore, most coarse sea-salt particles on the Antarctic plateau were likely to have originated from surface snow on the Antarctic continents. Figures 11 and 12 show that high Cl/Na ratios on the Antarctic plateau often corresponded to conditions with strong winds and drifting snow. Thus, sea-salt particles immediately after release from snow surface may have high Cl/Na ratios. Then, sea-salt particles in coarse mode might be modified gradually with reactive nitrogen oxides such as HNO_3 in the continental atmosphere during transport over the Antarctic continent.

Referee's comment: Page 11416, lines 25-29: This section appears diffuse and I do not understand what the authors try to tell us with this statement.

Reply from Authors: To simplify the statement, some sentences were removed from the text. The sentences were changed to

By contrast, S/Na ratios in fine sea-salt particles exceeded mostly 0.5 during the traverse. The high S/Na ratios in each sea-salt particle in fine mode imply that sulfates were formed on the fine sea-salt particles through heterogeneous reactions with gaseous sulfur species such as H_2SO_4 and SO_2.

Referee's comment: Page 11418, lines 20-21: I can see no reason for a "Supplementary" for just one figure, which can readily be presented in the main text!

Reply from Authors: Plots of Mg/Na ratio in fine mode were added to Figure 14. Some explanation was added into the main text.

Referee’s comment: Concluding remarks, Page 11422, line 9: sea salt modification (not fractionation) is meant here.

Referee’s comment: Exactly, “sea salt modification” is corrected here.

Other points such as typos were corrected on basis of the comments.

All modified sentences and words were marked in text of the revised manuscript.

The manuscript was checked by native English speaker again (FASTEKJAPAN: http://www.fastekjapan.com/).

Reply to Referee #2

We would like to thank useful comments for improvement of our manuscript. Statements were corrected on the basis of referee's comments as follows.

Referee's comment: Page 11403: The authors discuss the Junge-slope without i) explaining how this quantity should be interpreted in practice, ii) or performing a proper interpretation of the observed slopes. Very few people are familiar with Junge-slopes or their meaning, so this whole discussion is worth little without modifying the text to better consider the two issues mentioned above.

Author's reply: The Junge slope is often used as index of shape of aerosol size distribution in fine – coarse modes. For instance, higher (lower) Junge-slope values can be observed in cases of high (low) number concentrations in fine mode and/or low (high) concentrations in coarse mode, respectively.

Referee's comment: Section 3.5.2 contains a few errors that need to be corrected. First, particle growth rates rarely exceed 10 nm/hour outside urban areas, being rather closer to 1 nm/hour in remote areas. As a result, it practically impossible that particles grow into the coarse mode by condensation and coagulation in the continental atmosphere (lines 10-12 on page 11411). For the same reason, it seems very unlikely that new particle formation could explain larger fraction of even .ne (>200 nm) particles (lines 22-23 on page 11410). A much more plausible reason in both cases is that these particle very originally primary particles (e.g. sea salt, dust or other) which had accumulated enough sulfate by condensation or cloud-processing to be classified as sulfate particles.

Author's reply: Based on comments from Referees #1 and #2, the statements were changed in the text as follows.

Higher relative abundance of sulfate particles in the outgoing traverse is likely to result from (1) increase of the number concentrations of sulfate particles in fine mode by particle growth of ultrafine sulfate particles by hygroscopicity and cloud processes, (2) cloud processes, and (3) decrease of the number concentration of sea-salt particles and the modified sea-salt particles during the summer.

Such a high relative abundance of coarse sulfate particles was not observed in the boundary layer but often in the lower free troposphere over Syowa Station (Hara et al., 2013). Consequently, sulfate particles can be grown to coarse mode through (1) hygroscopic growth, (2) cloud processes, (3) heterogeneous sulfate formation and (4) coagulation and condensation of condensable vapors (e.g., H_2SO_4 gas) under conditions with the low number concentrations of pre-existing particles on the Antarctic continent.

Referee's comment: Third, it is incorrect to state that sulfate particles were dominant in coarse mode (line 13 on page 11410), as in many case sea salt particle accounted for more than half of the particles.

Author's reply: Description was changed to

"sulfate particles were one of major aerosol particles in coarse mode and dominant in fine modes."

Referee's comment: The authors need to be more careful when discussing the reaction of nitrogen com-pounds with sea salt during their measurements. While it is highly likely that nitrate explains most of the Cl loss not accounted by sulfate in these measurements, there are no data to support this statement. The authors should more explicitly bring up that Cl loss due to HNO3 or other nitrogen reactions is a plausible explanation rather than a fact (pages 11415-16, abstract). Especially, when one reads the abstract only, one easily gets the impression that also nitrogen compounds were measured in sampled particles.

Author's reply: Ternary plots of Na-S-Cl in sea-salt particles strongly suggested high contribution of acidic species other than $SO_4^{2-}$and $CH_3SO_3^-$ to sea-salt modification (Cl-loss). Plausible acidic species other than $SO_4^{2-}$and $CH_3SO_3^-$ for Cl loss from sea-salt particles are reactive nitrogen oxides such as HNO_3, N_2O_5, and NO_3 (e.g.., Hara et al., 1999), and organic acids (Kerminen et al., 2000; Laskin et al., 2012). Previous studies of aerosol chemistry in the Antarctic regions indicated that NO_3^- concentrations were higher than organic acids (oxalate, formate, and acetate) (Jourdain and Legrand, 2002; Rankin and Wolff, 2003; Legrand et al., 2004; Hara et al., 2010, Weller et al., 2002, 2007; Weller et al., 2011). Furthermore, higher concentrations of reactive nitrogen oxides (e.g., HNO3 and NO) were observed on the Antarctic continent and coasts during summer (Davis et al., 2004; Dibb et al., 2004; Jones et al., 2011). Therefore, heterogeneous NO_3^- formation on sea-salt particles might make an important contribution to sea-salt modification in inland areas during summer.

These descriptions were added to the main text. Also, statements in abstract were changed to

Horizontal features of Cl/Na ratios imply that sea-salt modification (i.e. Cl loss) occurred on the Antarctic continent during summer. Most sea-salt particles in the continental region near the coast were modified with acidic sulfur species such as SO_4^{2-} and $CH_3SO_3^-$. By contrast, acidic species other than the acidic sulfur species (likely NO_3^-) contributed markedly to sea-salt modification in inland area during the traverse.

Minor issues
Referee's comment: Page 11400, line 13: The cause-effect relationship does not sound correct here. I seems more plausible that wind causes turbulence than other way around.

Author's reply: The statement was changed to

In addition to diurnal features of wind speed, the wind speed increased because of cyclone approach

Referee's comment: Page 11404: The authors discuss possible errors in estimating aerosol mass concentration from OPC measurements. Two other issues should be mentioned here. First, the association of water also dilutes salts, so the assumed density of the particles is overestimated at high relative humidity. Second, how accurately the diameter obtained from OPC measurement correspond to that needed to calculate particle mass (particle mass equivalent diameter)?

Author's reply: Plausible errors in the estimation of aerosol mass concentrations were added in the text as follows;

In section 2-3-1:
OPC was calibrated using polystyrene latex particles with spherical shape and refractive index of 1.59–0i. Thus, size provided from OPC is "optically PSL-equivalent size".

In section 3-2:
Spherical shape and density were assumed in the estimation of aerosol mass

concentration. As mentioned above, diameters in OPC are “optically PSL-equivalent size”, so that the estimated aerosol volume means “PSL-equivalent volume” in this study.

Therefore, the estimated mass concentrations included masses of water in aerosol particles in this study. The presence of water in aerosol particles can cause overestimation of aerosol density and mass concentrations because of salt dilution by water.

Referee’s comment: Page 11412, line 18: Hara et al (2014) is not in the reference list.

Author’s reply: Paper of Hara et al (2014) is preparing for publication. Therefore, statement of “Hara et al (2014)” was removed from the text.

Referee’s comment: Page 11413, lines 5 and 7: I do not understand the notation M % (mean, N %).

Author’s reply: Descriptions of range and mean value of relative abundance were changed as follows;

The relative abundance of mineral particles ranged in n.d. – 14.6 % in coarse mode and n.d. – 0.4 % in fine mode during the incoming traverse, although the relative abundance ranged in n.d. – 5.7% in coarse mode and n.d. – 0.1 % in fine mode during the outgoing traverse. Mean relative abundance in coarse mode was 3.8 and 1.8 % in incoming and outgoing traverses, respectively, and that in fine mode was 0.1 % and 0.01 % in incoming and outgoing traverses.

Other points were corrected on the basis of the comments.

All modified sentences and words were marked in text of the revised manuscript.

The manuscript was checked by native English speaker again (FASTEKJAPAN: http://www.fastekjapan.com/).