Dear Dr. Shiraiwa,

We appreciate your helps to handle this review.

Our manuscript has been revised based on two reviewers' comments. We added new experimental data in the revised manuscript. We addressed all comments and attached a detailed point-by-point response as below. Please notice our responses marked by red color. We also uploaded the full manuscript with the revised parts indicated by red color. We hope that the revised manuscript can be accepted and published in ACP.

Correspondence and phone calls about the paper should be directed to Weijun Li at the following address, phone, and e-mail address:

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Best regards,
Sincerely yours,
Weijun Li on behalf of the coauthors

MS NO. acp-2015-385

We are grateful for the reviewer's comments. Those comments are all valuable and helpful for improving our paper. We answered the comments carefully and have made corrections in the submitted manuscript. The corrections and the responses are as following:

1. Authors discuss nitrate as coating materials on sea-salt particles in several sections (e.g., 4.1). However, there is no N signal in Figures 3-5, and authors mention that "N content cannot be directly measured but has been inferred based on the probable aerosol components". If substantial amounts of nitrate occur within the particles, N peak may arise between C and O in the EDX signals (e.g., Fig. 4 h and j), although it depends on the detection efficiency and the energy resolution on the EDX. I cannot see N in the mapping data in Fig. 7. SIMS data in Fig. 8 does not show the presence of nitrate as well. Although theoretically it will be likely that nitrate occurs on the coating, the main discussion should not be based on "the probable aerosol components." I suggest distinguishing between the result and discussion clearly, i.e., nitrate should be discussed only in the discussion with proper references. Also the occurrence of nitrate is not a direct evidence, and the relative sentences need to be revised (e.g., Page 16727 line 23).

Response 1: We appreciate the reviewer's comments. Also, we noticed there is absent about nitrate evidence in the ACPD paper. Based on the reviewer's comments, we carefully added new nanoSIMS experiments. Firstly, we generated laboratory $NaNO_3$ particles on silicon substrate. The new Figure S3 shows the $^{14}N^{16}O_2^-$ and $^{23}Na^{16}O^-$ can be good markers of $NaNO_3$. Secondly, we used these markers to analyze the ambient SSA particles. Ion mappings and line scans show that these aged SSA contain abundant $^{14}N^{16}O_2^-$ and $^{23}Na^{16}O^-$ instead of fresh SSA (Fig. 9). Therefore, we can make one solid conclusion which the aged SSA contain $NaNO_3$.

We have revised the text in section 2.3 as follows:

"Laboratory generated $NaNO_3$ particles on silicon substrate analyzed by nanoSIMS show that $^{14}N^{16}O_2^-$ and $^{23}Na^{16}O^-$ are their markers (Fig. S3)."

We have revised the text in section 4.1 as follows:

“Figure 9a shows $^{35}Cl^-$ in the NaCl core and minor $^{16}O^-$ and $^{32}S^-$ in the coating in fresh SSA. Figure 9b shows the absence of $^{35}Cl^-$ and the high intensity of $^{16}O^-$, $^{14}N^{16}O_2^-$, $^{32}S^-$, and $^{23}Na^{16}O^-$ in fully aged SSA. These results are completely consistent with the TEM and STEM observations in Figures 2, 4, and 8. Based on the mappings of $^{32}S^-$ (sulfate), $^{14}N^{16}O_2^-$ (nitrate), and $^{23}Na^{16}O^-$ in Figure 9, the nanoSIMS analysis provide direct evidence of Na_2SO_4 and $NaNO_3$ formation in fully aged SSA.”

We have revised the text (Page 16727, line 23) as follows:

“Integrated observations of individual SSA through the TEM, STEM, and nanoSIMS provided direct evidence of the occurrence of sulfate and nitrate in aged SSA in the arctic atmosphere.”

We have revised the text in section 5 as follows:

“NanoSIMS technology has been employed to obtain secondary ion intensity mappings of $^{12}C^-$, $^{16}O^-$, $^{12}C^{14}N^-$, $^{14}N^{16}O_2^-$, $^{32}S^-$, $^{35}Cl^-$, and $^{23}Na^{16}O^-$. $^{14}N^{16}O_2^-$ and $^{23}Na^{16}O^-$ mappings proved $NaNO_3$ formation in fully aged SSA.”

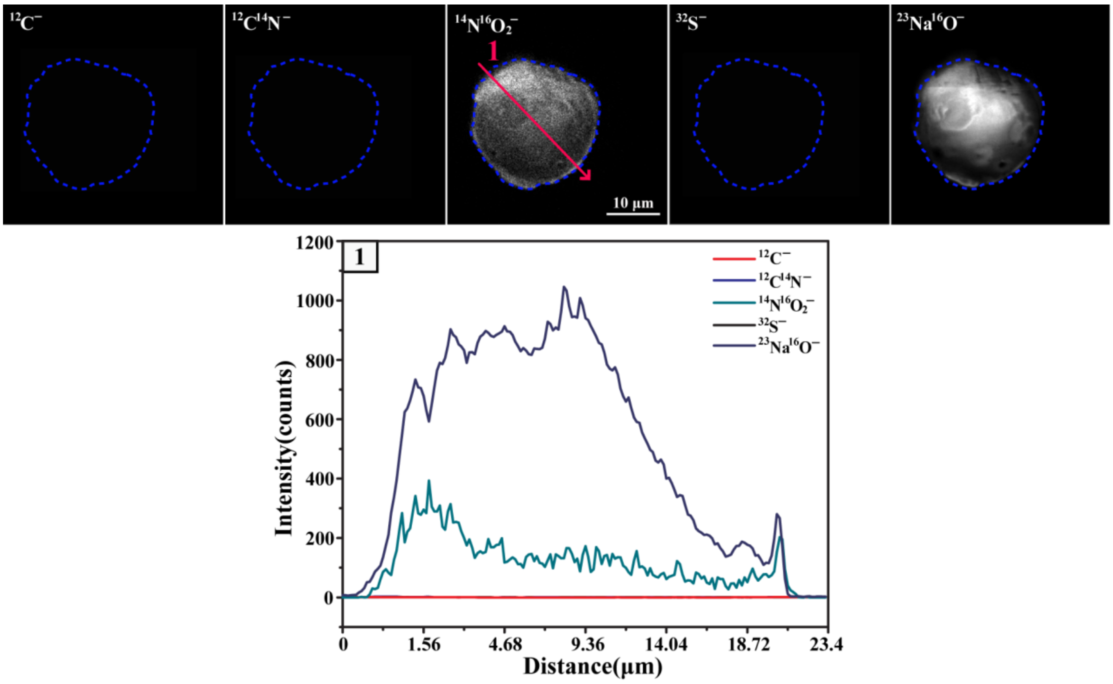

Figure S3. NanoSIMS-based ion intensity mappings. Mappings of $^{12}C^-$, $^{12}C^{14}N^-$, $^{14}N^{16}O_2^-$, $^{32}S^-$, and $^{23}Na^{16}O^-$ from laboratory generated $NaNO_3$ particle on silicon substrate. Line 1 represents the line scanning on the surface of individual particle.

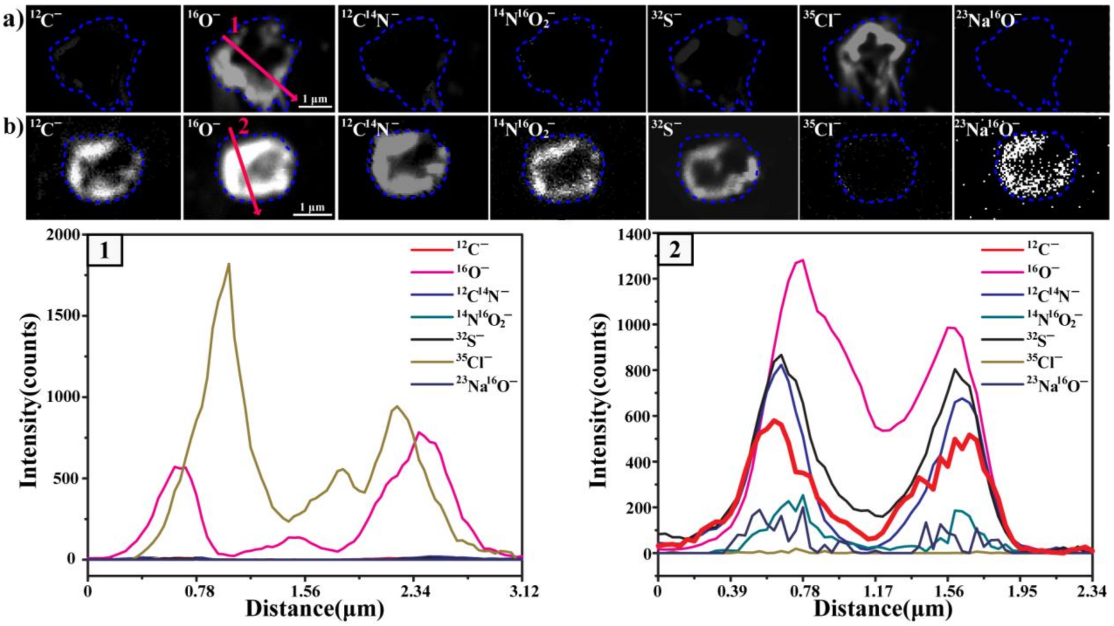

Figure 9. NanoSIMS-based ion intensity mappings. Mappings of $^{12}C^-$, $^{16}O^-$, $^{12}C^{14}N^-$, $^{14}N^{16}O_2^-$, $^{32}S^-$, $^{35}Cl^-$, and $^{23}Na^{16}O^-$ from one fresh SSA particle (a) and one fully aged SSA (b). Lines 1-2 represent the line scanning on the surfaces of individual particles. The red line represents the profile of $^{12}C^-$ in fully aged SSA.

2. Similar to nitrate, I am also wandering the occurrence of organic. The authors used $^{12}C^{14}N^-$ as an organic tracer. It seems to me that $^{12}C^{14}N^-$ may be a tracer of organonitrate or some specific types of organic, although I am not familiar with the technique. Please specify the availability of $^{12}C^{14}N^-$ as an organic tracer.

Response 2: We totally agree with the reviewer's comments. Similar to the question on nitrate, we did new nanoSIMS experiments including $^{12}C^-$ and $^{12}C^{14}N^-$ in SSA particles. We found $^{12}C^-$ and $^{12}C^{14}N^-$ ion intensity mappings have very similar distribution in individual particles. Based on the new experiment, we adopted $^{12}C^-$ as the tracer of organic matter. Figure 9 give some detail information of organic distribution following $^{12}C^-$ ion intensity mapping and line scan. We have revised "$^{12}C^-$" to replace "$^{12}C^{14}N^-$" in the appropriate text.

3. The authors classified sea-salt particles into fresh, partially aged, and fully aged ones based on morphology and chemical compositions. Is there any relation between the aging process and the back trajectory analysis? If not, it may not be appropriate to discuss compositional changes as particles age since the classification was made depending on the compositions but not aging, i.e., “it is shown that there is a major change of their internal structure and composition as the particles ageing (page 16724 line 24)” is not accurate because the particles aging was determined based on their internal structure and composition. Overall, it should be more careful to discuss the aging process unless the classification was determined based on the “aging.”

Response 3: As the reviewer’s requests, we re-analyzed the back trajectory. We found the particle ageing associated with the back trajectories of air masses. Please noticed that we revised Figure 6 and added new section 3.3 as follows:

“3.3 The SSA aging and back trajectories of air masses

Three-day (72h) back trajectories of air masses were generated using the HYSPLIT model at the Chinese Arctic Yellow River Station during August 3-23, 2012, at an altitude of 500 m above the sea level (Fig. 6). Most air masses originate in the Arctic Ocean, and are restricted to this vast marine region during the sampling periods. Figure 6 shows that two groups of back trajectories exhibit different ageing degree of SSA: One group originates from central Arctic Ocean and other one from North America and Greenland. Fractions of the fresh, partially aged, and fully aged SSA are 43.07%, 44.53%, and 12.41% in first group and 18.72%, 47.45%, 33.83% in second group, respectively (Fig. 6). As a result, air masses from North America and Greenland brought large amounts of aged SSA into the arctic area in summertime.”

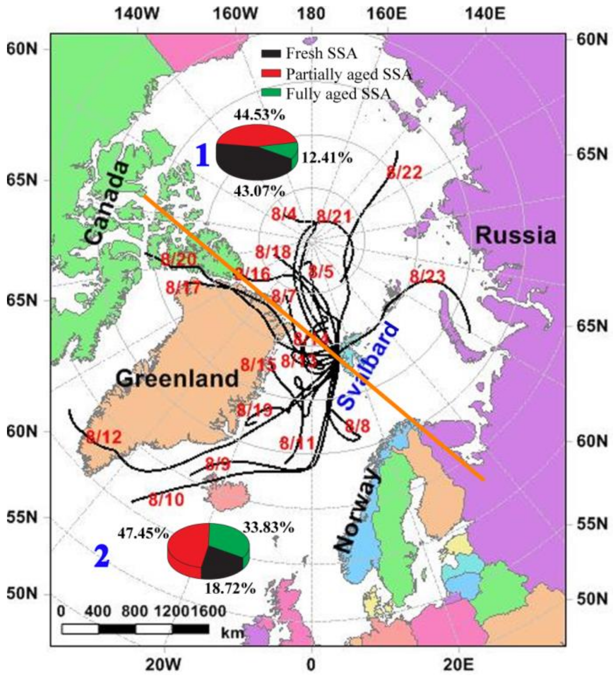

Figure 6. 72-h back trajectories of air masses at 500 m over Arctic Yellow River Station in Svalbard during 3-23 August, 2012, and arriving time was setting according to the sampling time. Air masses were divided into two groups by the yellow line: one group from central Arctic Ocean and other one from North America and Greenland. Pie charts showed the number fractions of the fresh, partially aged, and fully aged SSA.

We have revised the text (Page 16724, line 24) as follows:

"Using individual particle analysis of the three types of SSA, it is shown that there is a major change of their internal structure and composition"

4. Page 16715 Name and e-mail may not be consistent in the first corresponding author.

Response 4: It is our negligence and we are sorry about this. We have revised the text (Page 16715, Name and e-mail).

5. Page16718 Line 5: Recently, Laskin et al. (2012): : :. Here and elsewhere, authors refer Laskin et al. (2012). I suggest taking out "Recently" since it was published in 2012.

Response 5: Page16718 Line 5, Page16725 Line 22, and Page16727 Line 25, we delete "Recently" in the sentence.

6. Page16721 Line 21 (equation 1): I guess this equation is wrong (take out 4/3).

Response 6: We have revised the text (Page16721, Line 21) as follows:

$$A = \frac{4}{3}\pi r^2 = \frac{\pi d^2}{3} \rightarrow d = \sqrt{\frac{3A}{\pi}} \qquad (1)$$

7. Page 16729 line 11: "Comparisons of fresh and aged SSA in Fig. 8 suggest that these organic coatings likely took part in the chloride depletion during particles ageing." In Fig. 8 (and Fig. 7) authors show particle elemental mappings to show particle aging. However, they are different particles and do not show their aging process directly. Thus, the increasing or decreasing of elements may not reflect the aging process but just particle differences. Thus, it may be too strong to conclude "The chloride depletion in the SSA induced by the presence of organic matter should be incorporated into the atmospheric chemistry models for clean marine air (Page 16730 line 22)" from this study. At least, more careful discussion will be needed.

Response 7: We carefully made discussion as the reviewer's comments. In this study, we carefully evaluated our data and back trajectories of air masses. Only the chloride depletion in the SSA can provide the direct evidence about the particle ageing in this study. As a result, the additional sulfate, nitrate, and organic matter were added in aged SSA. Based on laboratory experiments and our analysis, the heterogeneous reactions on SSA with acids can be explained the phenomenon. In the laboratory experiments, H_2SO_4/SO_2, HNO_3/NO_x, and organic acids can react with NaCl particles (Laskin et al., 2003;Ault et al., 2013;Ghorai et al., 2014). To make solid conclusion, we make one new Na-Cl-O triangular diagram in Figure 5. Figure 5 gives general information about Cl depletion of the fresh, partially aged, and fully aged SSA. Three particle types in the triangular diagram display interesting distribution: the fresh SSA around the NaCl, the partially aged SSA in the center of triangular (including partial NaCl), the fully aged SSA around $NaNO_3$ and Na_2SO_4 (chloride full depletion).

We have revised the text in section 3.3 and 4.1 as follows:

"To summarize three types of SSA, we make one Na-Cl-O triangular diagram. Figure 5 gives general information about Cl depletion among the fresh, partially aged, and fully aged SSA. Three particle types in the triangular diagram display interesting distribution: the fresh SSA around the NaCl, the partially aged SSA in the center of triangular (including partial NaCl), the fully aged SSA around $NaNO_3$, and Na_2SO_4 (chloride full depletion)."

"Na-Cl-O triangular diagram further shows that Cl in SSA has been depleted and O content increases likely through additional chemical reactions (Fig. 5)."

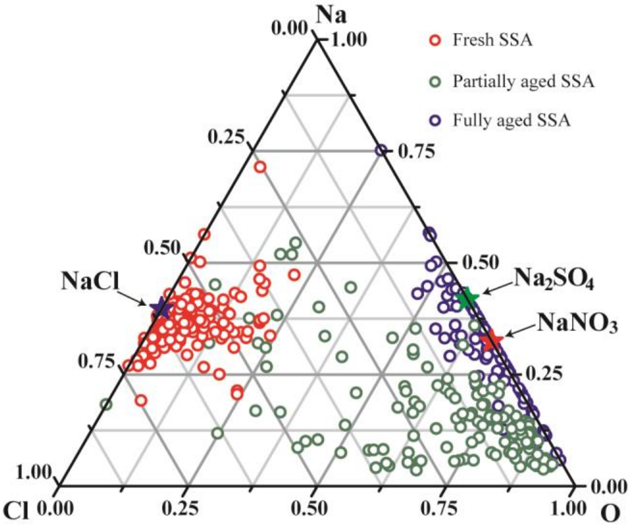

Figure 5. Triangular diagram of Na-Cl-O showing EDX data of elemental composition of 405 SSA. Three stars represent elemental composition of pure NaCl, Na_2SO_4, and $NaNO_3$, respectively.

8. Figure 3: Fig. 3j shows O signal for $MgCl_2$ in EDX but Fig. 3k does not have O for CaSO4. Why?

Response 8: Because $MgCl_2$ is close to $CaSO_4$ in the individual particle, O signal in $MgCl_2$ is from the nearby $CaSO_4$. For O signal in $CaSO_4$, it is our negligence and we are sorry about this. We selected suitable EDX data of $MgCl_2$ and $CaSO_4$ in Figure 2 as follows:

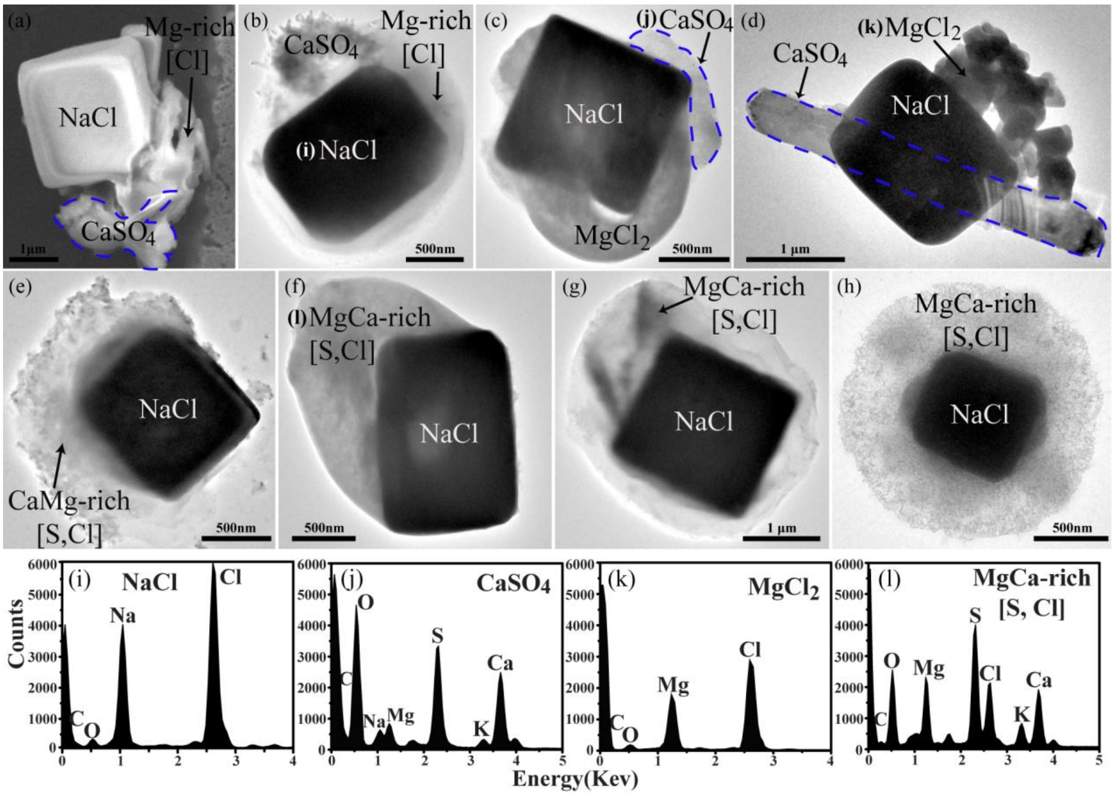

Figure 2. Morphology and EDX spectra of the typical fresh SSA. (a) One SEM image, (b)-(h) TEM images, and (i)-(h) EDX spectra of NaCl, $MgCl_2$, $CaSO_4$, and MgCa-rich. The main anionic elements are shown in the square brackets.

9. Please specify the cutoff size in aerodynamic diameter for the sampler if any. The cutoff sizes will influence the particle size distributions.

Response 9: We have revised the text in section 2.1 as follows:

"The collection efficiency of the impactor is 50% for particles with an aerodynamic diameter of 0.3 μm and almost 100% at 0.5 μm if the density of particles is 2 g cm^{-3}"

10. N mapping may be artifact since it was determined without detecting N in EDX. It can come from C and O since N peak is between these elements. Please check it. The TEM images are rotated comparing to the mapping images. Can it be fixed?

Response 10: We didn't fully understand the reviewer's comments. We try to answer them. In the EDX spectra, we could not determine N signal (Figs. 2-4). However, we can obtain the N mapping in the scanning TEM (Fig. 8). In the dark-field mode of

TEM, there is the lowest noise and highest resolution for light element. Therefore, N mapping is believable in Figure 8, although it cannot supply the quantitative data. Fortunately, we had new nanoSIMS experiments to provide direct evidence about the nitrate (Figs. 9 and S3).

11. Figure S2: Please check if the R^2 value is correct. It looks the value (R^2=0.9888) is too high for the plotting.

Response 11: We checked the R^2. Previously, we used OriginPro 8 to process the AFM data, R^2=0.9888. We used microsoft excel 2010 to calculate it again. The value is R^2=0.765. We thank the reviewer's comments.

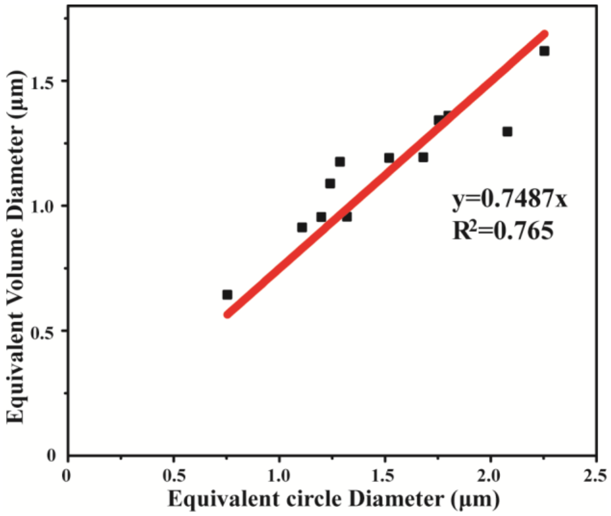

Figure S2. The correlation of equivalent circle diameter (d) and equivalent volume diameter (D) obtained by AFM.

References:

Ault, A. P., Guasco, T. L., Ryder, O. S., Baltrusaitis, J., Cuadra-Rodriguez, L. A., Collins, D. B., Ruppel, M. J., Bertram, T. H., Prather, K. A., and Grassian, V. H.: Inside versus outside: ion redistribution in nitric acid reacted sea spray aerosol particles as determined by single particle analysis, J. Am. Chem. Soc., 135, 14528-14531, doi:10.1021/ja407117x, 2013.

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We are grateful for Dr. Tang's comments. Those comments are all valuable and helpful for improving our paper. We answered the comments carefully and have made corrections in the submitted manuscript. The corrections and the responses are as following:

1. I fully agree with the comments made by ref. 1. Especially, nitrate has not been detected but inferred. Authors should provide a convincing explanation why nitrate has not been detected by any of these techniques they used, and justify how nitrate was inferred from their measurement.

Response 1: We appreciated Dr. Tang's comments. We made the new experiments after your comments and provided the more strong evidences. Please see our answers and new data in the response 1 of the reviewer#1's comments.

2. Page 16724, line 10-12: it is claimed that because aged SSA particles are more spherical compared to fresh ones, aged SSA particles tend to be droplets. I disagree with it. Although the conclusion can be true, the observation that aged particles are more spherical is only related to crystallization processes during dehumidification, and is not necessarily related to these phases at high RH.

Response 2: Yes, we fully agree with the reviewer. Here we only describe morphology of dry particles on the substrate. At high RH, they all become spherical shape in the atmosphere after the DRH.

We have revised the text (Page 16724, line 10-12) as follows:

"The fully aged SSA (Fig. 4) on the substrate become more round compared with fresh SSA (Fig. 2) and partially aged SSA (Fig. 3)."

3. Page 16727, line 1-3: I am not convinced that $NaNO_3$ coating totally determines the hygroscopic and optical properties of aged SSA particles. At most the measurements may suggest that aged SSA particles are more likely to be droplets in the ambient air, compared to fresh SSA particles. To make such a strong claim, the authors are required to present data of hygroscopic and optical properties for both fresh and aged SSA particles. In addition, I think even fresh SSA particles are likely to be droplets for ambient RH of 56-94%. Though pure NaCl has a DRH of 77%, its ERH is much lower. By the way, even fresh SSA particles should not be pure NaCl, but containing other salts which are contained in sea water.

Response 3: We agree with your comments. We could not presume the particle phase in real atmosphere based on their compositions on the substrate. However, we did one hygroscopic experiment to understand how particle compositions change their hygroscopic properties.

We added new hygroscopic experimental data for three typical SSA in supporting information (Fig. S4). Hygroscopic properties of individual SSA in Figure S4 show fresh, partially aged, and fully aged SSA start to grow at 69%, 65%, and 60%, respectively. The results show that nitrate coatings in SSA can change hygroscopic properties of particle surfaces. In addition, we carefully made some corrections about the tone.

We have revised the text (Page 16716, line 17-19) as follows:

"These new findings indicate that this mixture of organic matter and $NaNO_3$ on particle surfaces likely determines their hygroscopic and optical properties."

We have revised the text (Page 16726, line 15-18) as follows:

"In the partially aged particles, the new coating containing $MgSO_4$, $Mg(NO_3)_2$, and $NaNO_3$ (Fig. 3) likely remained as a supersaturated liquid coating on the surface of the ambient SSA in the arctic area (Zhao et al., 2006;Li et al., 2008;Woods et al., 2010)."

We have revised the text (Page 16727, line 1-3) as follows:

"Hygroscopic experiments of individual SSA exhibit that the surfaces of partially and fully aged SSA have earlier deliquescence than that of fresh SSA based on their hygroscopic growth on the substrate. The results indicate that the nitrate coatings likely influence particle surface deliquescence (Fig. S4)."

We have revised the text (Page 16727, line 5-8) as follows:

"As a result, some partially and fully aged Arctic SSA had liquid surfaces in ambient air (56~94% RH) and that this liquid amounted to certain amounts of water in these aerosol particles."

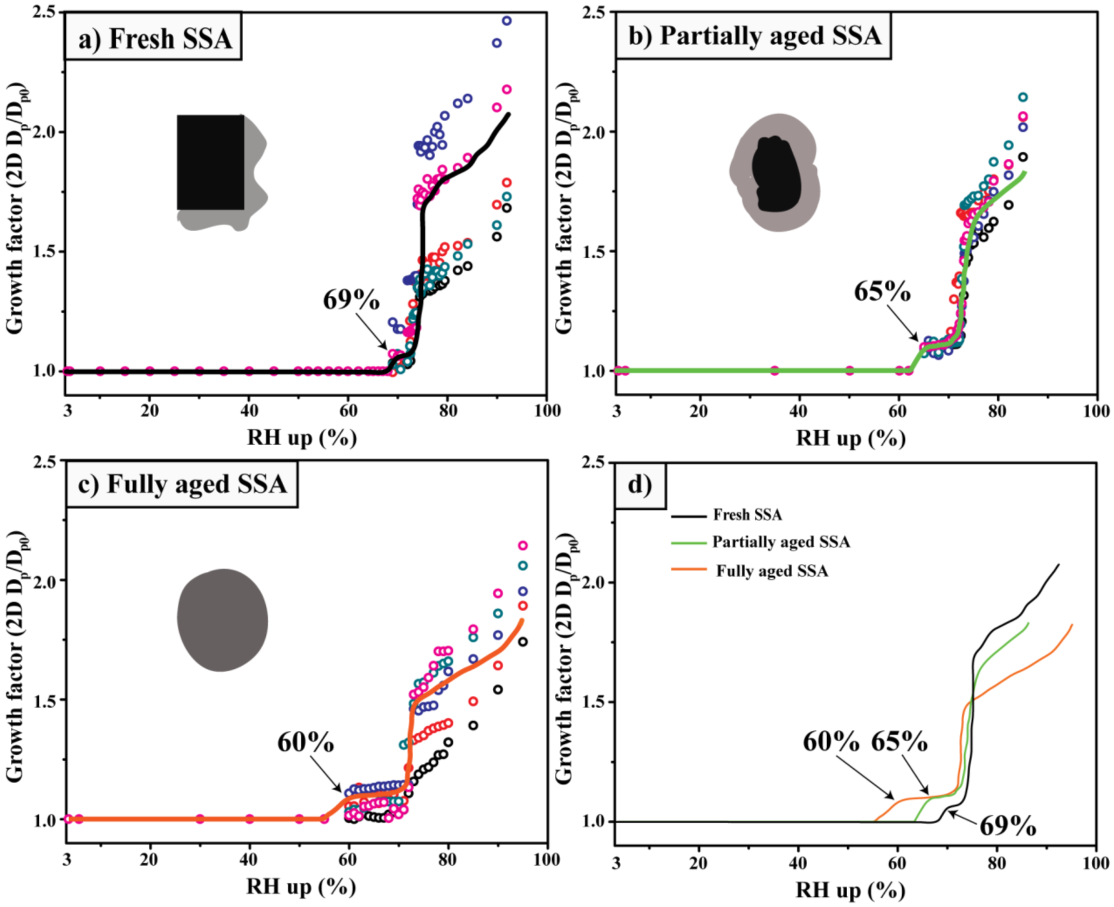

Figure S4. Deliquescence process of fresh SSA (a), partially aged SSA (b), and fully aged SSA (c) with different colors for different particles. The lines show the hygroscopic growth of individual SSA. The relative humidity for three typical SSA is 3-92%, 3-85%, and 3-95%, respectively.

4. Page 16727, line 19-24: if surface reactions produce Cl_2, the photolysis of Cl_2 will produce Cl atoms, further enhancing the photochemical reactivity. I am not sure why it will reduce the overall photochemical reactivity. More explanations should be provided.

Response 4: These reactions are beyond our study. We carefully modified it based on the references (De Haan et al., 1999;Knipping et al., 2000;von Glasow, 2008a;Thornton et al., 2010).

We have revised the text in section 4.2 as follows:

“On the other hand, these surface reactions of SSA could affect the photochemical reactivity in the Arctic air because they release gaseous halogen species (De Haan et al., 1999;Knipping et al., 2000;von Glasow, 2008b;Thornton et al., 2010).”

5. Page 16727, line 17-19: one of the four reactions will produce $ClNO_2$; instead, it is formed in the reaction of N_2O_5 with Cl^-.

Response 5: The reaction is beyond our current study. We deleted this sentence.

6. Page 16729, line 2-3: what the author found is that organic compounds are coated on aged SSA particles, and I am not sure that it is equal to phase separation used in atmospheric chemistry community. Since the editor is an expert in this field, I will leave the decision to the editor.

Response 6: From $^{12}C^-$ line scan, we did find $^{12}C^-$ signal higher in outer layer. We carefully compare it with laboratory experiment published in JACS (Ault et al., 2013) and field experiment published in JGR (Laskin et al., 2012).

7. Figure 6: I feel “volume equivalent diameter” is more proper than “equivalent spherical diameter”.

Response 7: We have revised “equivalent volume diameter” to replace “equivalent spherical diameter” in the article and figures.

8. Page 16722, line 18: “don’t experience” should be “have not experienced”. Although the paper is not difficult to follow, it will benefit a lot if it can be revised and edited by a native speaker.

Response 8: We have revised it. The native speaker helped to smooth the context.

“The fresh SSA refer to particles which have not experienced any atmospheric chemical modification after emission.”

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Ault, A. P., Guasco, T. L., Ryder, O. S., Baltrusaitis, J., Cuadra-Rodriguez, L. A., Collins, D. B., Ruppel, M. J., Bertram, T. H., Prather, K. A., and Grassian, V. H.: Inside versus outside: ion redistribution in nitric acid reacted sea spray aerosol particles as determined by single particle analysis, J. Am. Chem. Soc., 135, 14528-14531, doi:10.1021/ja407117x, 2013.

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von Glasow, R.: Atmospheric chemistry: pollution meets sea salt, Nature Geosci., 1, 292-293, 2008b.

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Sea salt aerosols as a reactive surface for inorganic and organic acidic gases in the arctic troposphere

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Abstract

Sea salt aerosols (SSA) are dominant particles in the arctic atmosphere and determine the polar radiative balance. SSA react with acidic pollutants that lead to changes of physical and chemical properties of their surface, which in turn alter their hygroscopic and optical properties. Transmission electron microscopy with energy-dispersive X-ray spectrometry was used to analyze morphology, composition, size, and mixing state of individual SSA at Ny-Ålesund, Svalbard in summertime. Individual fresh SSA contained cubic NaCl coated by certain amounts of $MgCl_2$ and $CaSO_4$. Individual partially aged SSA contained irregular NaCl coated by a mixture of $NaNO_3$, Na_2SO_4, $Mg(NO_3)_2$, and $MgSO_4$. The comparison suggests the hydrophilic $MgCl_2$ coating in fresh SSA likely intrigued the heterogeneous reactions at the beginning of SSA and acidic gases. Individual fully aged SSA normally had Na_2SO_4 cores and an amorphous coating of $NaNO_3$. Elemental mappings of individual SSA particles revealed that as the particles ageing Cl gradually decreased but the C, N, O, and S content increased. $^{12}C^-$ mapping from nanoscale secondary ion mass spectrometry indicates that organic matter increased in the aged SSA compared with the fresh SSA. $^{12}C^-$ line scan further shows that organic matter was mainly concentrated on the aged SSA surface. These new findings indicate that this mixture of organic matter and $NaNO_3$ on particle surfaces likely determines their hygroscopic and optical properties. These abundant SSA as reactive surfaces absorbing inorganic and organic acidic gases can shorten acidic gas lifetime and influence the possible gaseous reactions in the arctic atmosphere, which need to be incorporated into atmospheric chemical models in the arctic troposphere.

1 Introduction

The arctic atmosphere was long believed to be an extremely clean background laboratory to research aerosol chemical processes, transport of atmospheric aerosols, and their impact on global climate (Law and Stohl, 2007). In the last decades, however, arctic temperatures have increased at twice the global average rate (Serreze and Francis, 2006), resulting in a dramatic decrease of Arctic pack ice (Lindsay et al., 2009). This arctic climate change has been attributed to the increase of greenhouse gases in the troposphere (Vavrus, 2004) and to anthropogenic emissions of air pollutants from the middle latitudes (Barrie, 1986;Iziomon et al., 2006;Law and Stohl, 2007). In particular, the "Arctic Haze" phenomenon caused by the long-range transport of anthropogenic emissions (e.g., organic acids, H_2SO_4/SO_2, and HNO_3/NO_x) from lower latitudes has received increasing attention in the last thirty years (Heintzenberg, 1980;Shaw, 1995;Law and Stohl, 2007).

Various aerosol particles from industrial, urban, and marine emissions occur in the arctic atmosphere (Goto-Azuma and Koerner, 2001;Ghorai et al., 2014). Black carbon as one solar absorber in the troposphere and in the snow or ice (Hegg et al., 2009) can amplify the change of the arctic climate (Sand et al., 2013). In addition, H_2SO_4/SO_2 and HNO_3/NO_x from anthropogenic sources in middle latitudes are transported into the central arctic area (Law and Stohl, 2007), where they react with sea salt aerosols (SSA) (Hara et al., 2003;Geng et al., 2010;Sierau et al., 2014). SSA have reactive surfaces that can easily participate in heterogeneous and multiphase chemical reactions (Rossi, 2003) and play a significant role in the global S and N cycle (Pósfai et al., 1994;Sierau et al., 2014). These aged SSA not only affect incoming solar radiation by scattering or absorbing directly (Murphy et al., 1998), but also can serve as cloud condensation nuclei (CCN) or ice nuclei (IN) and further alter cloud properties (Hu et al., 2005;Leck and Svensson, 2015). It was also proved that such cloud changes cause 40% of the arctic warming (Vavrus, 2004). Understanding the chemical composition of the arctic SSA is critical to understand how they affect the polar climate (Hara et al., 2003).

SSA have been intensively studied in both laboratory and field experiments in coastal areas (O'Dowd et al., 1997;O'Dowd and De Leeuw, 2007;Yao and Zhang, 2011;Li et al., 2011b;Laskin et al., 2012;Ault et al., 2012;Ghorai et al., 2014). In laboratory studies Ault et al. (2013a) suggested spatial redistribution of the cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) between core and surface after heterogeneous reaction of SSA and nitric acids. Deliquescence-mode experiments with mixed NaCl/$MgSO_4$ aerosol particles show that Mg salts (e.g., $MgSO_4$ and $MgCl_2$) concentrated in the surface can easily take up water and lower the deliquescence point of NaCl particles (Woods et al., 2010). Hara et al. (2003) suggested that most SSA play a pivotal pole in the lower troposphere (< 3 km) and result in noticeable depletion of chlorine in the arctic. Laskin et al. (2012) found that SSA may effectively react with organic acids, leaving behind particles depleted in chloride and enriched in the corresponding organic salts in one polluted coastal area. Organic acids can react with SSA and change their hygroscopicity in polluted continental air (Ghorai et al., 2014), which can alter their heterogeneous reactions and CCN activity (Laskin et al., 2012). In light of the limited microscopic observations of arctic aerosols, at least two questions have not been answered. Firstly, detailed information about ageing processes of SSA surfaces has not been determined in the arctic atmosphere. Secondly, to what degree do organic acids react with SSA in the clean atmosphere? This knowledge is critical to understand how small amounts of anthropogenic gases (e.g., organic acids, H_2SO_4/SO_2, and HNO_3/NO_x) affect the hygroscopic and optical properties of SSA in the clean arctic atmosphere.

To characterize individual SSA collected on August 3-23, 2012, at the Chinese Arctic Yellow River Station, we applied different microscopic techniques with resolution down to the nanometer scale: transmission electron microscopy with energy-dispersive X-ray spectrometry (TEM/EDX), scanning electron microscopy (SEM), scanning TEM (STEM), and atomic force microscopy (AFM), and nanoscale secondary ion mass spectrometry (nanoSIMS). The different types of individual SSA were identified based on their morphology and composition. Elemental and ion mappings revealed mixing properties of different species in individual SSA which further participated in chemical reactions in the clean Arctic atmosphere. The dual aims of our study are to explain the need to understand the complexity of realistic atmospheric SSA and to provide fundamental experimental data to understand heterogeneous reactions of SSA in the clean arctic atmosphere.

2 Experiments

2.1 Sampling

Svalbard is an archipelago in the Arctic Ocean consisting of Spitsbergen, Bear Island, and Hopen, which together cover about 62,000 km^2. Ny-Ålesund, whose geographical coordinates are 78°55′N, 11°56′E, is situated on the west coast of Spitsbergen and is an international center of scientific research and environmental monitoring in the central Arctic.

Aerosol samples were collected from 3 to 23 August, 2012, using an individual particle sampler at the Chinese Arctic Yellow River Station, Ny-Ålesund (Fig. S1). We use copper TEM grids coated with carbon film (carbon type-B, 300-mesh copper, Tianld Co., China) to collect aerosols by a single-stage cascade impactor with a 0.5-mm-diameter jet nozzle at a flow rate of 1.0 L min^{-1}. The collection efficiency of the impactor is 50% for particles with an aerodynamic diameter of 0.3 μm and almost 100% at 0.5 μm if the density of particles is 2 g cm^{-3}. The sampling duration of each sample varied from twenty minutes to two hours depending on the aerosol dispersion on the film that was estimated by optical microscopy after the sampling. Then we placed the grids in sealed, dry, plastic capsules to prevent contamination. Finally, the samples were stored in a desiccator at 25 ^{o}C and 20±3% relative humidity (RH) until analysis (Li et al., 2011a).

According to the sampling time and sample quality, 23 aerosol samples were selected for analysis with TEM. During the sampling periods, temperatures were 1.6~7.3 ^{o}C; RH, 56~94%; air pressure, 997.0~1020.7 hPa; and sampling wind speeds, 0~8.9 m s^{-1}. Detailed sampling information can be found in Table S1.

2.2 Electron microscopic analyses

Individual particle samples were examined by a JEOL JEM-2100 transmission electron microscopy operated at 200 kV with energy-dispersive X-ray spectrometry

(TEM/EDX) and scanning electron microscopy (SEM; Philips XL30) operated at a 20 kV accelerating voltage and a 80 μA filament. EDX spectra were examined within a maximum time of 30 s to minimize potential beam damage and efficiently collect particle elemental composition. TEM grids were made of copper (Cu) and covered by a carbon-reinforced substrate, so Cu had to be excluded from the quantitative analyses of the particles while residual C content was detected and overestimated in EDX spectra of individual particles. Elemental composition, morphology, size distribution, and mixing state have been studied by the TEM/EDX. Both submicron and supermicron particles occur on the TEM grids: coarser particles occur near the center, and finer particles are on the periphery (Li and Shao, 2009). To be more representative, 4-5 areas from the center to periphery of the sampling spot were chosen to analyze all the particles. Altogether we analyzed 1577 aerosol particles to understand the details of their mixing states, both internal and external. We used iTEM software to analyze the TEM images and obtained area, circularity, perimeter, and equivalent circle diameter of individual aerosol particles.

Some typical aerosol particles were analyzed for elemental mapping with a JEOL JEM-2100F TEM with scanning TEM (STEM) operation mode. Elemental mappings were collected in the annular dark-field imaging mode, with the electron beam focused on a corresponding spot of the sample but then scanned over this area in a raster. Elemental mapping has become an important tool in individual particle analysis in the recent years (Ault et al., 2012;Li et al., 2013a;Li et al., 2013b), because it clearly displays the distribution of the detectable elements within each particle.

2.3 NanoSIMS analysis

Individual aerosol particles were analyzed using a nanoscale secondary ion mass spectrometer (nanoSIMS) 50L (CAMECA Instruments, Geneviers, France), an ultra-high vacuum technique for surface and thin-film analysis at the Institute of Geology and Geophysics, Chinese Academy of Sciences. In this study, $^{12}C^-$, $^{16}O^-$, $^{12}C^{14}N^-$, $^{14}N^{16}O_2^-$, $^{32}S^-$, $^{35}Cl^-$, and $^{23}Na^{16}O^-$ ions in individual particles were obtained when the Cs^+ primary ion beam caused the ionization of atoms within the particles. Furthermore, ion intensity mappings of individual particles with nanometer resolution can show the distribution of different ions. $^{12}C^-$ represents the organic matter in individual particles that excludes the contribution from the carbon substrate. Laboratory generated $NaNO_3$ particles on silicon substrate analyzed by nanoSIMS show $^{14}N^{16}O_2^-$ and $^{23}Na^{16}O^-$ are their markers (Fig. S3).

2.4 AFM analysis

Atomic force microscopy (AFM) with a tapping mode analyzed aerosol particles under ambient conditions. AFM, a digital NanoscopeIIIa Instrument, can detect the three-dimensional morphology of particles. The AFM settings contain imaging forces between 1 and 1.5 nN, scanning rates between 0.5 and 0.8 Hz, and scanning range sizes at 10 μm with a resolution of 512 pixels per length. After the AFM analysis, composition of the same particles was confirmed by TEM, with twelve SSA particles analyzed by this method. The NanoScope analysis software can automatically obtain bearing area (A) and bearing volume (V) of each analyzed particle according to the following formula.

$$A = \frac{4}{3}\pi r^2 = \frac{\pi d^2}{3} \rightarrow d = \sqrt{\frac{3A}{\pi}} \qquad (1)$$

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{\pi D^3}{8} \rightarrow D = \sqrt[3]{\frac{6V}{\pi}} \qquad (2)$$

Where *d* is the equivalent circle diameter and *D* the equivalent volume diameter.

Additionally, we know the relation between *d* and *D* is $D = 0.7487 \times d$, as shown in Fig. S2. As a result, equivalent circle diameter (*d*) of individual aerosol particles measured from the iTEM software can be further converted into equivalent volume diameter (*D*) based on this relationship.

3 Results

3.1 Types and size distribution of Arctic aerosol particles

Based on their different morphology and composition, aerosol particles were divided into four major categories: sea salt (Fig. 1A-a), S-rich (OC-coating) (Fig. 1A-b), Ca/Mg-S/N/Cl (Fig. 1A-c) and mineral (Fig. 1A-d). TEM observations indicated that SSA were most abundant from 100 nm to 10 μm in the summer arctic atmosphere. Figure 1B shows that the relative abundance of SSA in the samples was about 72% of the total aerosols. This result is consistent with the dominant SSA in different seasons reported for the arctic atmosphere (Hara et al., 2003;Geng et al., 2010).

3.2 The microscopic characterization and elements of SSA

Based on their morphology and composition, we can further identify three types of SSA: fresh SSA, partially aged SSA, and fully aged SSA.

3.2.1 Fresh SSA

The fresh SSA refer to particles which have not experienced any atmospheric chemical modification after emission. TEM and SEM images clearly show that individual fresh SSA include the cubic NaCl core with $MgCl_2$ and $CaSO_4$ coating (Fig. 2). Figure 2i shows that the NaCl core only contains Na and Cl with their ionic concentration ratio (Na/Cl) close to 1:1. The coating contains appropriate quantities of Mg, Ca, S, O and Cl, which could be defined as $CaSO_4$, $MgCl_2$, and other species (Figs. 2j, k, l). NaCl particles surrounded by the Mg-rich and Ca-rich coatings have been inferred by SEM and TEM (Pósfai et al., 1994;Murphy et al., 1998;Hara et al., 2003;Geng et al., 2010), but the details about the coatings have not been revealed in the Arctic atmosphere. In this study, the high-resolution TEM and SEM images displayed the accurate mixing structures of NaCl and other species. Here we identified two kinds of fresh SSA: one, a NaCl core encased by a distinct coating of $CaSO_4$ and Mg-rich ($MgCl_2$) materials (e.g., Figs. 2a-d); and another, a NaCl core encased by a mixture of Mg-rich and Ca-rich materials (e.g., Figs. 2e-f).

3.2.2 Partially aged SSA

Partially aged SSA, we define as those particles that experience atmospheric chemical modifications on their surfaces but retain the NaCl core. Figures 3a-f show that individual partially aged SSA clearly include NaCl core and coating. The morphology of the partially aged SSA differ from the fresh ones as shown in the TEM images of Figs. 2 and 3. Figure 3 shows that the core still keeps the crystalline phase of NaCl with its irregular shape and that the coatings mainly consist of Na, Mg, Ca, K, O, and S with either negligible or minor Cl. Typical Cl-depletion phenomena suggest that the SSA likely underwent chemical ageing in the atmosphere, as below:

$MgCl_{2(s\ or\ aq)} + HNO_{3(g\ or\ aq)} \rightarrow Mg(NO_3)_{2(aq)} + HCl_{(g\ or\ aq)}$ (R1)

$MgCl_{2(s\ or\ aq)} + H_2SO_{4(g\ or\ aq)} \rightarrow MgSO_{4(aq)} + HCl_{(g\ or\ aq)}$ (R2)

$NaCl_{(s\ or\ aq)} + HNO_{3(g\ or\ aq)} \rightarrow NaNO_{3(aq)} + HCl_{(g\ or\ aq)}$ (R3)

$NaCl_{(s\ or\ aq)} + H_2SO_{4(g\ or\ aq)} \rightarrow Na_2SO_{4(aq)} + HCl_{(g\ or\ aq)}$ (R4)

(s, solid; aq, aqueous; and g, gaseous)

Similar chemical reactions on SSA have been detected in both coastal air and laboratory experiments (Allen et al., 1996;Gard et al., 1998;Kouyoumdjian and Saliba, 2006;Ault et al., 2013a). These heterogeneous chemical reactions significantly change the morphology and composition of SSA. Our results suggest that the $MgCl_2$ coatings in fresh SSA were converted into a more complex coating mixture of $MgSO_4$, $Mg(NO_3)_2$, Na_2SO_4, and $NaNO_3$ in partially aged SSA.

3.2.3 Fully aged SSA

In fully aged SSA the NaCl core has been completely transformed into $NaNO_3$ and Na_2SO_4 through atmospheric heterogeneous chemical reactions with acidic gases. Figure 4 shows that the fully aged SSA have completely lost their NaCl core, suggesting that the Cl in SSA was completely depleted through heterogeneous chemical reactions, such as reactions (R1)-(R4). The rod-like Na_2SO_4 aggregates comprising the core were frequently internally mixed with $NaNO_3$. TEM study indicates that Na_2SO_4 and $NaNO_3$ are crystalline and amorphous materials, respectively. The fully aged SSA (Fig. 4) on the substrate become more round compared with fresh SSA (Fig. 2) and partially aged SSA (Fig. 3).

3.3 The SSA ageing and back trajectories of air masses

To summarize three types of SSA, we make one Na-Cl-O triangular diagram. Figure 5 gives general information about Cl depletion among the fresh, partially aged, and fully aged SSA. Three particle types in the triangular diagram display interesting distribution: the fresh SSA around the NaCl, the partially aged SSA in the center of triangular (including partial NaCl), the fully aged SSA around $NaNO_3$, and Na_2SO_4 (chloride full depletion).

Three-day (72h) back trajectories of air masses were generated using the HYSPLIT model at the Chinese Arctic Yellow River Station during August 3-23, 2012, at an altitude of 500 m above the sea level (Fig. 6). Most air masses originate in the Arctic Ocean, and are restricted to this vast marine region during the sampling periods. Figure 6 shows that two groups of back trajectories exhibit different ageing degree of SSA: One group originates from central Arctic Ocean and other one from North America and Greenland. Fractions of the fresh, partially aged, and fully aged SSA are 43.07%, 44.53%, and 12.41% in first group and 18.72%, 47.45%, 33.83% in second group, respectively (Fig. 6). As a result, air masses from North America and Greenland brought large amounts of aged SSA into the arctic area in summertime.

3.4 Size distribution of individual SSA

Figure 7 shows size distributions of the fresh, partially aged, and fully aged SSA. The peaks of fresh and partially aged SSA are 0.68 μm and 1.30 μm, respectively, and the fully aged ones display a broad size range from 0.9 μm to 2.0 μm (Fig. 7). Our results show that the average particle sizes gradually increase from fresh SSA, partially aged SSA, to fully aged SSA. Therefore, dry and wet deposition of aerosol particles could be changed following the degree of the particles ageing.

4 Discussion

4.1 Sulfate and nitrate formation in individual SSA

TEM observations classified the SSA into fresh, partially aged, and fully aged SSA in the arctic atmosphere. Using individual particle analysis of the three types of SSA, it is shown that there is a major change of their internal structure and composition. The STEM further determined elemental mappings of Na, Mg, Ca, Cl, S, O, C, and N in the three kinds of SSA. Elemental mapping can clearly display the elemental distribution within each particle, which indicates the possible heterogeneous chemical reactions on their surfaces (Conny and Norris, 2011;Ault et al., 2012). Figure 8 shows that Cl content decreases and S, O, C and N contents increase from partially aged (particle B) to fully aged SSA (particle C). Na-Cl-O triangular diagram further shows that Cl in SSA has been depleted and O content increases likely through additional chemical reactions (Fig. 5). Figure 9a shows $^{35}Cl^-$ in the NaCl core and minor $^{16}O^-$ and $^{32}S^-$ in the coating in fresh SSA. Figure 9b shows the absence of $^{35}Cl^-$ and the high intensity of $^{16}O^-$, $^{14}N^{16}O_2^-$, $^{32}S^-$, and $^{23}Na^{16}O^-$ in fully aged SSA. These results are completely consistent with the TEM and STEM observations in Figures 2, 4, and 8. Based on the mappings of $^{32}S^-$ (sulfate), $^{14}N^{16}O_2^-$ (nitrate), and $^{23}Na^{16}O^-$ in Figure 9, the nanoSIMS analysis provide direct evidence of Na_2SO_4 and $NaNO_3$ formation in fully aged SSA. As a result, sulfate and nitrate accumulated in SSA through atmospheric chemical reactions (e.g., reactions (R1)-(R4)) in the arctic area, which has been observed in polluted air by Laskin et al.(2012). These mapping results from STEM and nanoSIMS are consistent with the TEM/EDX results shown in Figs. 2-4 and with investigators who found that individual SSA in the Arctic air contained certain amounts of sulfate or nitrate by SEM/EDX and aerosol time-of-flight mass spectrometry (ATOFMS) (Hara et al., 2003;Geng et al., 2010;Sierau et al., 2014). However, we found that individual aged particles simultaneously contained sulfate and nitrate, suggesting individual SSA underwent heterogeneous reactions with different acidic gases during ageing processes in the arctic atmosphere. A number of studies found that a large fraction of SSA internally mixed with sulfate and nitrate occurred from coastal to background marine air and from equatorial to high latitudes (Andreae et al., 1986;Pósfai et al., 1994;Middlebrook et al., 1998;Hara et al., 2003;Geng et al., 2010;Li et al., 2011b;Yao and Zhang, 2011;Laskin et al., 2012). Interestingly, we noticed that fully aged SSA (Fig. 8C) had an elevated carbon content, suggesting that organic matter might occur in the aged SSA (the details in section 4.2). Laskin et al. (2012) showed that SSA can react with secondary organic acids and result in formation of organic salts in the polluted air.

Na mappings show that Na is absent in the coating of fresh SSA (Fig. 8A) but is present in minor amounts in the coating of partially aged SSA (Fig. 8B), which is consistent with the EDX results as shown in Figs. 2-3. In contrast, Mg, S, and O are absent from the core of fresh SSA (Fig. 8A) but are present in certain amounts within the core of partially aged SSA (Fig. 8B). Therefore, we can deduce that $MgCl_2$ coatings of the fresh SSA firstly reacted with acidic gases through chemical reactions (R1) and (R2) as the fresh SSA were transformed into the partially aged SSA. The presence of $MgCl_2$ coatings in the fresh SSA is particularly interesting because it is known to readily deliquesce at a considerably lower point (33% RH at 298 K) than that of NaCl (75%) (Wise et al., 2009). We conclude, therefore, that this $MgCl_2$ coating consistently allowed an aqueous layer to coat the fresh SSA in the Arctic atmosphere, because the ambient RH (56~94%) exceeded the deliquescence point. Despite the relatively low concentration of $MgCl_2$ in SSA, the liquid surface significantly enhances heterogeneous reactions rates through the uptake of acidic gases (e.g., H_2SO_4/SO_2, and HNO_3/NO_x) (Liu et al., 2007). Microscopic observations suggest that $MgCl_2$ on fresh SSA likely initiated and promoted the heterogeneous reactions between SSA and acidic gases. To our knowledge, this is the first demonstration of the influence of minor $MgCl_2$ in individual SSA in field studies, although this phenomenon has been reported in laboratory experiments (Zhao et al., 2006;Liu et al., 2007;Wise et al., 2009). In addition, $MgCl_2$ appears to have greater importance in individual Arctic SSA than elsewhere because the Mg^{2+}/Na^{+} ratio in SSA increases following a temperature decrease (Hara et al., 2012). In the partially aged particles, the new coating containing $MgSO_4$, $Mg(NO_3)_2$, and $NaNO_3$ (Fig. 3) likely remained as a supersaturated liquid coating on the surface of the ambient SSA in the arctic area (Zhao et al., 2006;Li et al., 2008;Woods et al., 2010). Therefore, the Mg-salts in fresh and partially aged SSA are important surfactants to speed up particles ageing in the arctic area.

In this study we found an abundance of fully aged SSA in this arctic area (Figs. 4-6). Ault et al. (2013a) found that the Na^{+}, Mg^{2+} and Ca^{2+} in individual SSA undergo a spatial redistribution after heterogeneous reaction with nitric acid in the laboratory. We noticed a similar phenomenon in which Na, Mg, and Ca mappings in particle C were different from particles A and B (Fig. 8). Na is enhanced at the surface; Mg and Ca tend to concentrate in the individual particle center. Figure 8C shows that carbon intensity becomes strong in fully aged SSA, similar to the C-rich coating in Figs. 4c-d. These results suggest that the aged SSA probably contain organic matter (the details in section 4.2). In addition, most of the fully aged SSA have a Na_2SO_4 core coated with $NaNO_3$ (with minor $Mg(NO_3)_2$ and $MgSO_4$) (Fig. 4). Hygroscopic experiments of individual SSA exhibit that the surfaces of partially and fully aged SSA have earlier deliquescence than that of fresh SSA based on their hygroscopic growth on the substrate. The results indicate that the nitrate coatings likely influence particle surface deliquescence (Fig. S4). In the laboratory, the pure $NaNO_3$ can take up water starting at 25% RH and grow continuously with increasing RH (Lee and Hsu, 2000). Hu et al. (2010) also illustrated that $NaNO_3$ did not exhibit obvious deliquescence phenomenon in the hygroscopic experiment. As a result, some partially and fully aged Arctic SSA had liquid surfaces in ambient air (56~94% RH) and that this liquid amounted to certain amounts of water in these aerosol particles. Park et al. (2014) supplied the evidence of water in arctic particles through the hygroscopicity and volatility tandem differential mobility analyzer. The hygroscopic growth of particles can cause 1.6 to 3.7 times more negative aerosol direct radiative effects (Sand et al., 2013) than particles without it.

4.2 Organic matter in aged SSA

Integrated observations of individual SSA through the TEM, STEM, and nanoSIMS provided direct evidence of the occurrence of sulfate and nitrate in aged SSA in the arctic atmosphere. Laskin et al. (2012) showed that SSA effectively reacted with organic acids in polluted coastal air, leaving behind particles depleted in chloride and enriched in the corresponding organic salts. Moreover, substitution of Cl in SSA by weak organic acids was suggested in the laboratory by Ma et al. (2013). However, whether weak organic acids participated in the chloride depletion remains uncertain in the clean arctic air.

NanoSIMS technology has been adopted to characterize organic matter in SSA through $^{12}C^-$ and $^{12}C^{14}N^-$ mappings (Fig. 9). $^{12}C^-$ mapping of fresh SSA indicates extremely small amounts of organic matter in its coating (Fig. 9a). Tervahattu et al. (2002) found that organic films on SSA are common in fresh marine aerosols because of bursting bubbles from the spay of the waves. Quinn et al. (2015) also found that fresh SSA are internally mixed with organic matter in the northeastern Atlantic atmosphere using proton nuclear magnetic resonance (^{1}HNMR). In comparison with fresh SSA in Figure 9a, the $^{12}C^-$ intensity of the aged SSA in Figure 9b was much enhanced. The only explanation is that more organic matter from the atmosphere was incorporated into the aged SSA. Similar phenomena in aged SSA have been observed by laser mass spectrometry at Cape Grim and the amounts of additional sulfate and organic matter in individual particles may be an indication of particles ageing (Middlebrook et al., 1998). Additionally, with increasing organic matter in SSA, their morphology and crystallization behavior changes (Ault et al., 2013b).

Interestingly, $^{12}C^{-}$ line scan in aged SSA further indicates that organic matter is mostly restricted to their surfaces (Fig. 9b). The near edge X-ray absorption fine structure spectroscopy (NEXAFS) carbon K-edge spectrum of the organic phase reveals a dominant contribution from carboxylic acids on the surface of the aged SSA (Laskin et al., 2012). We further found organic matter internally mixed with nitrate on the surface for aged SSA. This finding supports the results from laboratory experiments and conforms to predictions of liquid-liquid phase separation theory (Ault et al., 2013a). As a result, we obtained one conceptual model based on these above findings summarizing the possible SSA ageing processes in the arctic atmosphere (Fig. 10).

The nanoSIMS analyses of the aged SSA in the arctic air show that their surface layers commonly contain organic matter. The organic layer may influence trace gas uptake, and subsequently impact trace gas budgets of O_3 and NO_2 in the arctic (McNeill et al., 2006). This is the first demonstration of organic-coated SSA in clean arctic air, which extends the application of heterogeneous reactions on aerosol particles (Fig. 10). Comparisons of fresh and aged SSA in Fig. 9 suggest that these organic coatings likely took part in the chloride depletion during particles ageing. The chloride depletion in the SSA induced by the presence of organic acids should be incorporated into the atmospheric chemistry models for clean marine air, in addition to the coastal urban regions reported by Laskin et al. (2012). Randles et al. (2014) reported that NaCl internally mixed with organic matter can reduce radiative cooling substantially compared to pure NaCl aerosol in the laboratory. In addition, how the organic layer influences hygroscopic and optical properties of the aged SSA in realistic atmospheres remains unknown. Our measurements make clear the need to understand SSA's complexity in arctic air.

In summary, our results indicate that formation of sulfate, nitrate, and organic salts in the SSA can remove trace gases (e.g., organic acids, H_2SO_4/SO_2, and HNO_3/NO_x) in the arctic air, which were mostly emitted by various anthropogenic sources from middle latitudes (Law and Stohl, 2007;Chang et al., 2011). On the one hand, the results of these heterogeneous reactions could change the CCN or IN abilities, optical properties, and further dry and wet deposition of SSA. On the other hand, these surface reactions of SSA could affect the photochemical reactivity in the Arctic air because they release gaseous halogen species (De Haan et al., 1999;Knipping et al., 2000;von Glasow, 2008;Thornton et al., 2010).

5 Conclusions

TEM observations indicated that SSA were most abundant from 100 nm to 10 μm in the summer arctic atmosphere, accounting for about 72% of the total aerosol particles. Three types of SSA, fresh SSA, partially aged SSA, and fully aged SSA, were identified based on their morphology and composition. The fresh SSA particles exhibited a single core-shell structure. Containing only Na and Cl, the core consisted of the cubic NaCl crystal with the coating of Mg, Ca, S, O and Cl, identified as $CaSO_4$ and $MgCl_2$. Individual partially aged SSA particles consisted of the single irregularly shaped NaCl core coated with Na, Mg, Ca, K, N, O, and S, with or without minor Cl, suggesting a single Cl-depletion phenomenon in the formation of partially aged SSA. The fully aged SSA lack the NaCl core, suggesting that the Cl in SSA was completely depleted through heterogeneous chemical reactions. Nonetheless, most fully aged SSA consist of the Na_2SO_4 core with the amorphous $NaNO_3$ coating.

STEM further determined the elemental mappings of Na, Mg, Ca, Cl, S, O, C, and N in the three kinds of SSA. We found that Cl content decreases and S, O, C and N contents increase along with particles ageing from partially to fully aged SSA. NanoSIMS technology has been employed to obtain secondary ion intensity mappings of $^{12}C^-$, $^{16}O^-$, $^{12}C^{14}N^-$, $^{14}N^{16}O_2^-$, $^{32}S^-$, $^{35}Cl^-$, and $^{23}Na^{16}O^-$. $^{14}N^{16}O_2^-$ and $^{23}Na^{16}O^-$ mappings proved $NaNO_3$ formation in fully aged SSA. These results show that sulfate and nitrate formed in SSA through atmospheric chemical reactions in arctic area. In addition, $MgCl_2$ coating on fresh SSA can induce heterogeneous reactions between SSA and acidic gases because $MgCl_2$ is known to readily deliquesce at a considerably lower point (33% RH at 298 K) than that of NaCl (75%). The partially and fully aged SSA were expected to have liquid surfaces ($MgSO_4$, $MgNO_3$, and $NaNO_3$) in arctic ambient air (56~94% RH); such surfaces contain substantial amounts of water, so the coating contents were conducive to accelerate the heterogeneous reactions. $^{12}C^-$ mapping of individual fresh SSA obtained by nanoSIMS indicate extremely small amounts of organic matter in the coating of the particle, although this organic matter was somewhat enhanced in the aged SSA. We also found that organic matter was mostly limited to the particle surface.

The composition of the SSA and their internal heterogeneity likely have important effects on their hygroscopic and optical properties, dynamics of phase separations, and heterogeneous reaction with inorganic and organic acidic gases. These microscopic observations for SSA provide insights into the system of gas-aerosol-climate in the arctic atmosphere.

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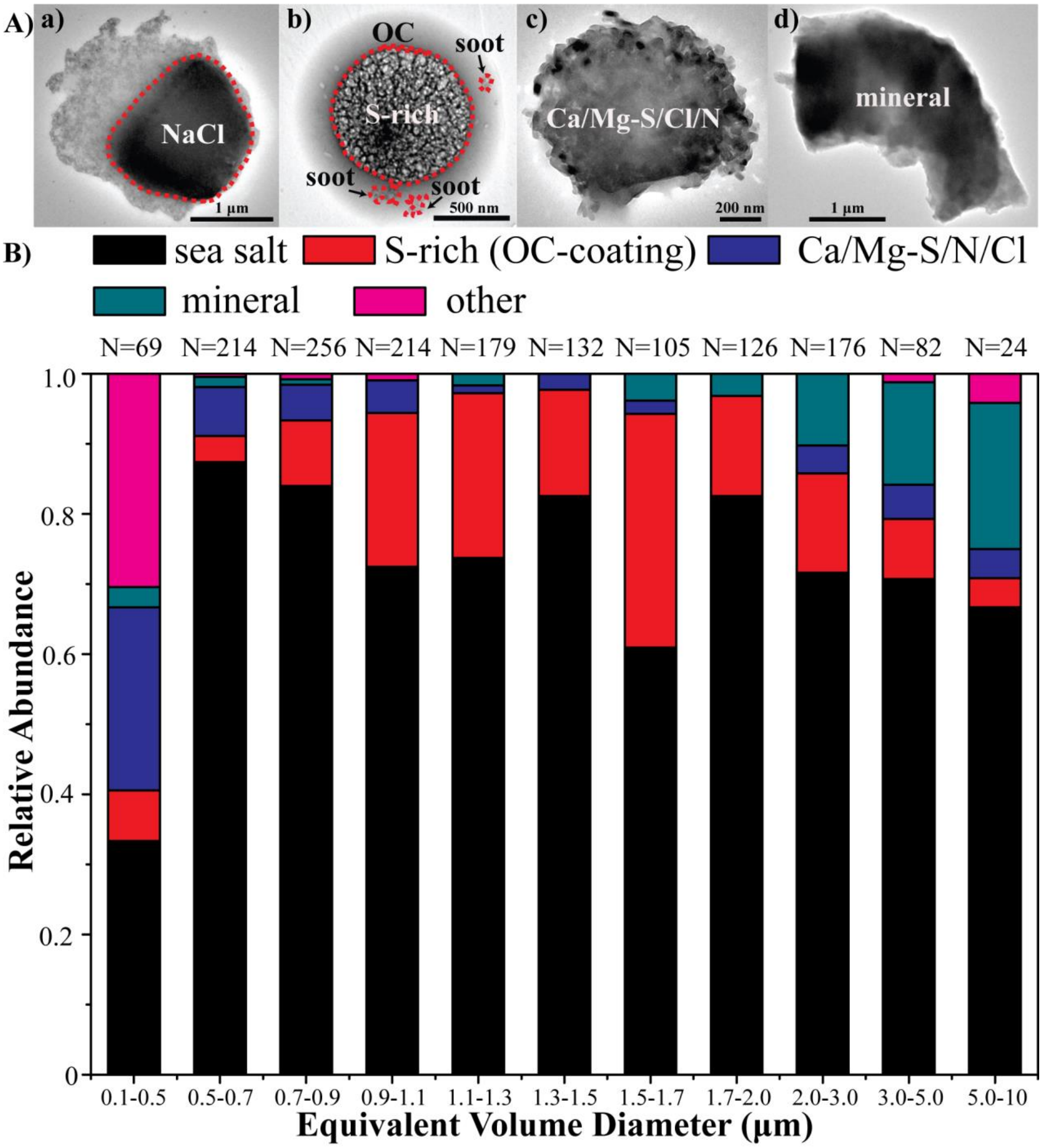

Figure 1. Morphology and relative abundances of typical individual aerosol particles in summertime Arctic samples: (A) TEM images of four types of aerosol particles, (B) relative abundances of different particle size ranges. The number of the analyzed particles in different size ranges is shown above each column.

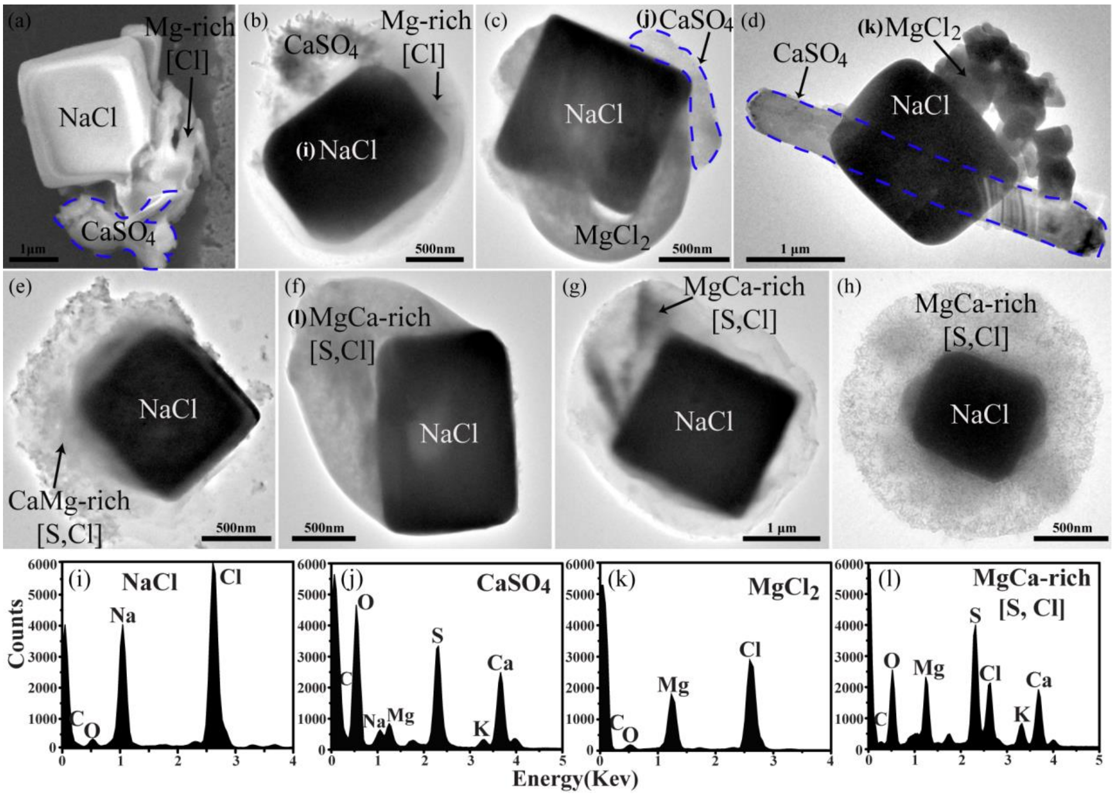

Figure 2. Morphology and EDX spectra of the typical fresh SSA. (a) One SEM image, (b)-(h) TEM images, and (i)-(h) EDX spectra of NaCl, $MgCl_2$, $CaSO_4$, and MgCa-rich. The main anionic elements are shown in the square brackets.

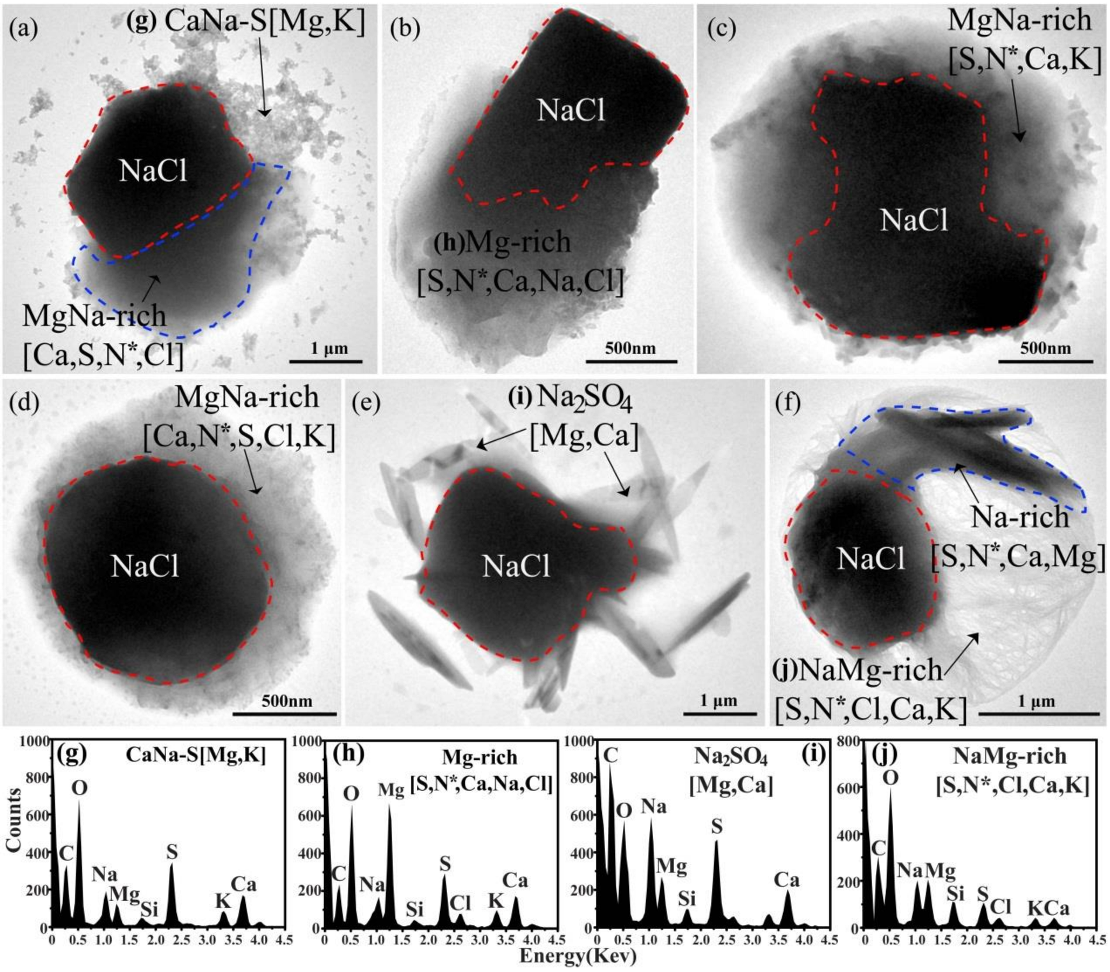

Figure 3. TEM images of typical partially aged SSA and EDX spectra of their coatings. (a-b) NaCl partially surrounded by the mixed species, containing Mg, Ca, Na, S, O, N and minor Cl; (c-d) NaCl completely surrounded by the mixed species with Mg, Ca, Na, S, O, N and minor Cl; (e-f) The rod-like Na_2SO_4 particles (minor Mg, and Ca) associated with NaCl. (g-j) The EDX spectra of one selected area in the internally mixed coating, including Na, Ca, Mg, S, and O with minor Cl and K. N cannot be directly measured but inferred based on elemental composition in aerosols.

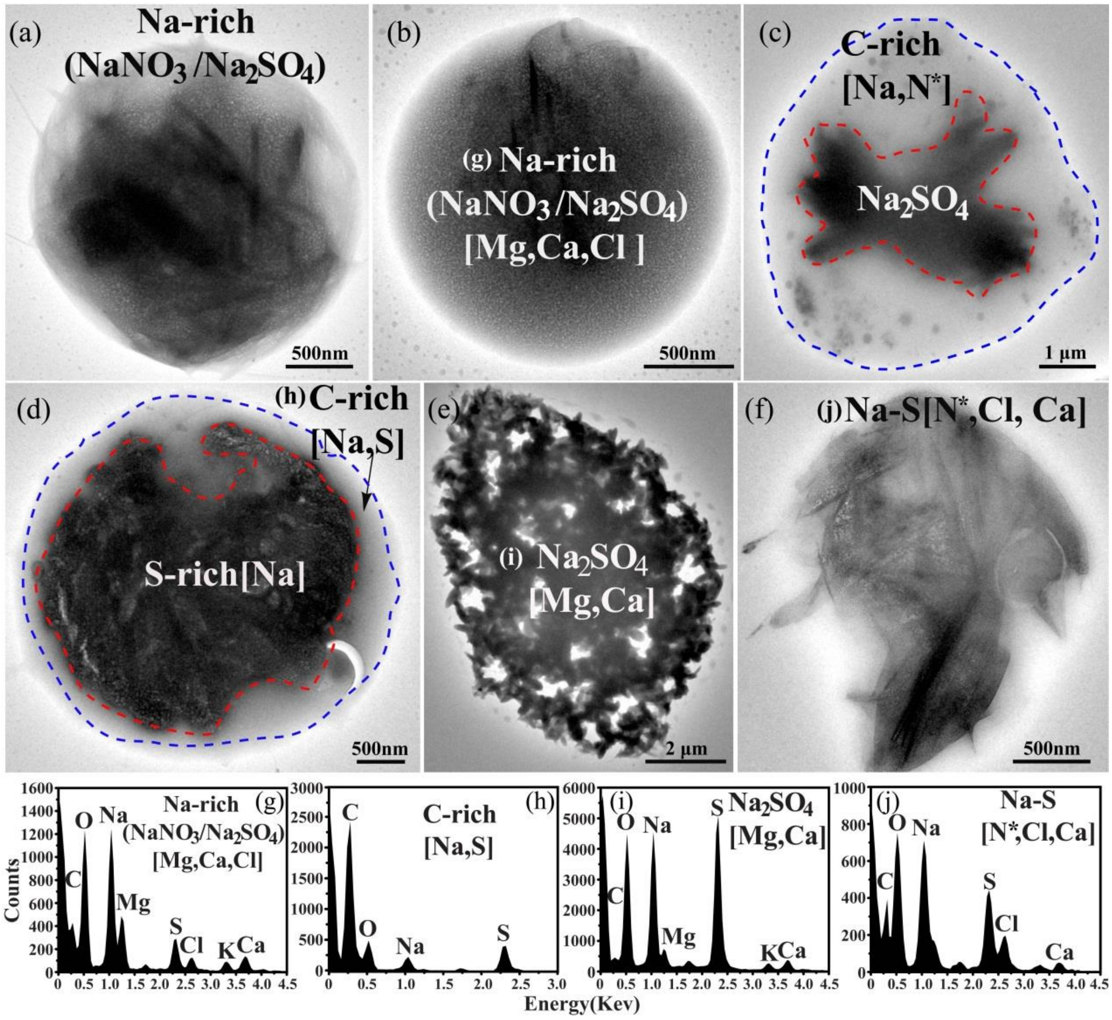

Figure 4. TEM images and EDX spectra of the typical fully aged SSA. Major species are shown in parentheses, and minor elements are in square brackets. (a-b) This Na-rich particle contains mostly Na, O, N, and S. The rod-like aggregates are Na_2SO_4 and the species of no-defined shape are $NaNO_3$. The $NaNO_3$-containing coating is more sensitive to the strong electron beam than the Na_2SO_4. (c-d) Na-rich particles mainly contain C, N, O, Na, and S. One typical transparent coating with high C and minor O, Na, S or N, was stable under a strong electron beam, suggesting a possible organic coating. (e-f) The particles mainly contain Na, O, and S. Many small rod-like Na_2SO_4 gather together to form one particle. (g-j) EDX spectra of one selected part within individual SSA marked in TEM images. N cannot be directly measured but inferred based on elemental composition in aerosols.

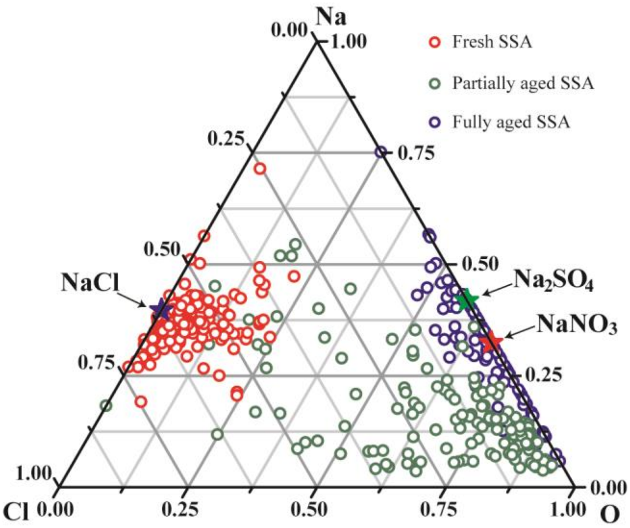

Figure 5. Triangular diagram of Na-Cl-O showing EDX data of elemental composition of 405 SSA. Three stars represent elemental composition of pure NaCl, Na_2SO_4, and $NaNO_3$, respectively.

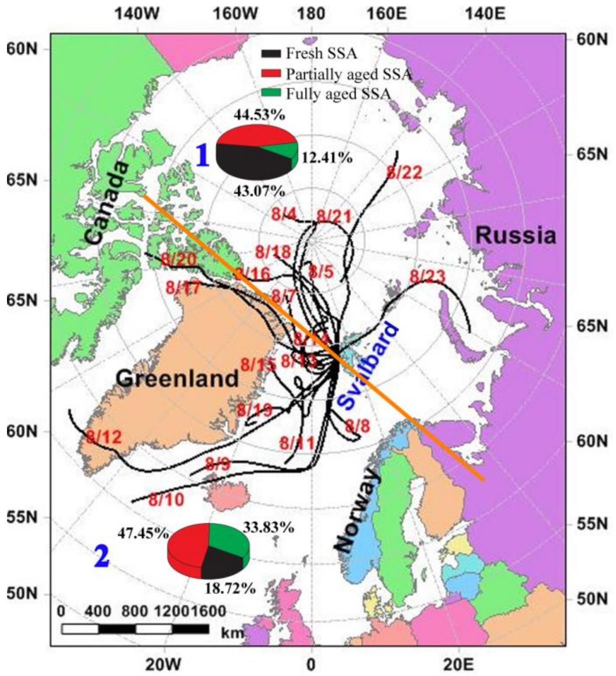

Figure 6. 72-h back trajectories of air masses at 500 m over Arctic Yellow River Station in Svalbard during 3-23 August, 2012, and arriving time was setting according to the sampling time. Air masses were divided into two groups by the yellow line: one group from central Arctic Ocean and other one from North America and Greenland. Pie charts showed the number fractions of the fresh, partially aged, and fully aged SSA.

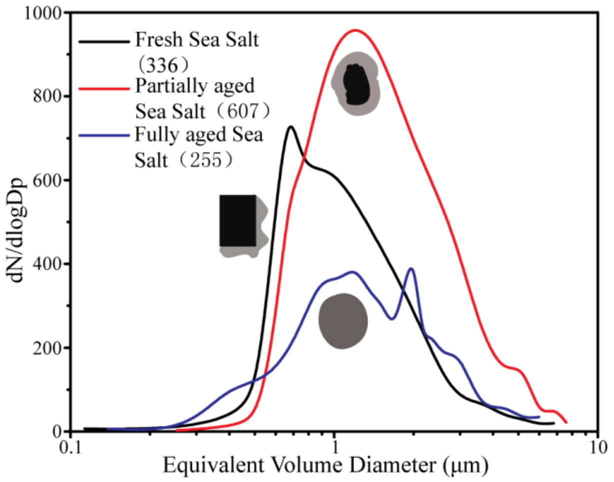

Figure 7. Size distributions of 336 fresh, 607 partially aged, and 255 fully aged SSA collected in Arctic summer. The SSA with diameters lower than 100 nm were not considered in this study.

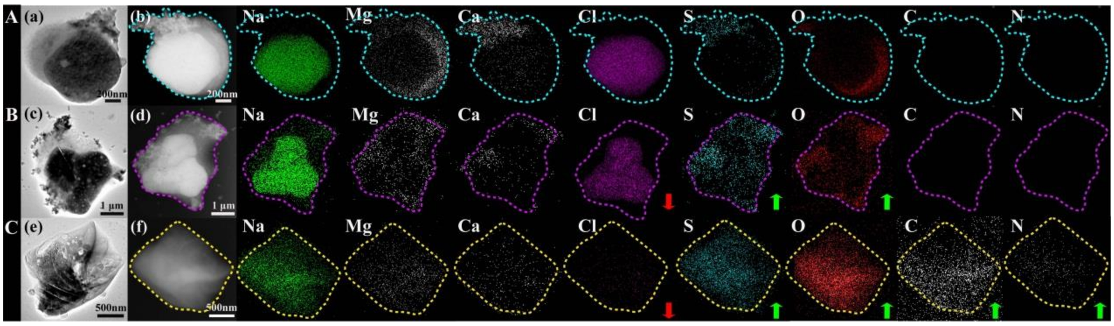

Figure 8. Bright and dark-field TEM images of the fresh, partially aged, and fully aged SSA and elemental mapping of Na, Mg, Ca, Cl, S, O, C, and N. (A) One fresh SSA particle, (B) One partially aged SSA particle, (C) One fully aged SSA particle. The dot intensity represents elemental concentration within an individual particle. The arrows in particles B and C represent increase or decrease of elemental concentration compared to the particle A.

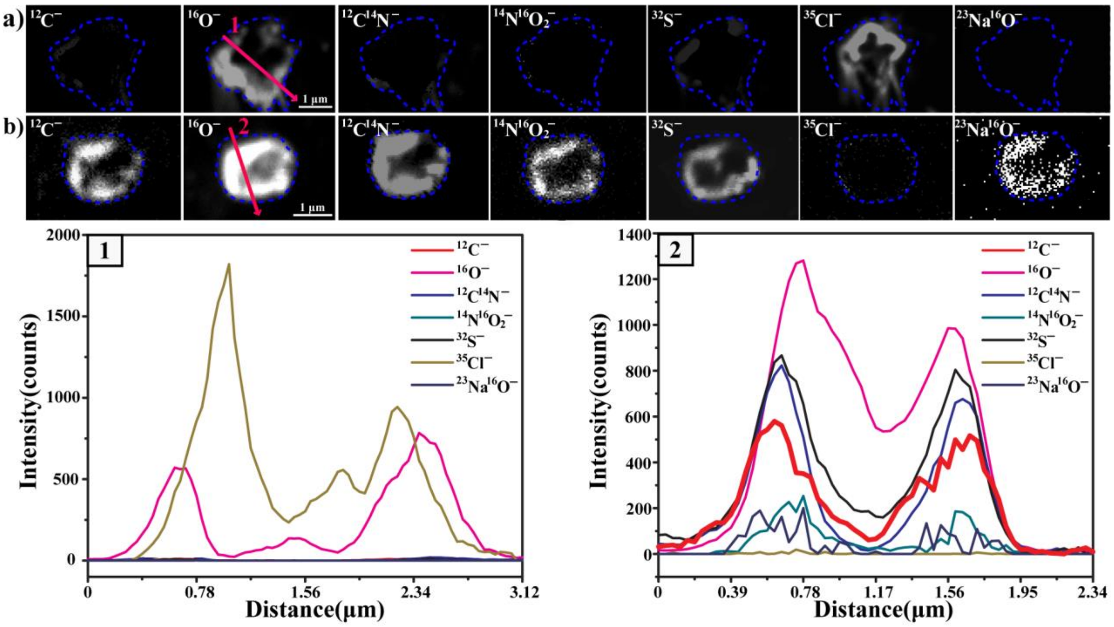

Figure 9. NanoSIMS-based ion intensity mappings. Mappings of $^{12}C^-$, $^{16}O^-$, $^{12}C^{14}N^-$, $^{14}N^{16}O_2^-$, $^{32}S^-$, $^{35}Cl^-$, and $^{23}Na^{16}O^-$ from one fresh SSA particle (a) and one fully aged SSA (b). Lines 1-2 represent the line scanning on the surfaces of individual particles. The red line represents the profile of $^{12}C^-$ in fully aged SSA.

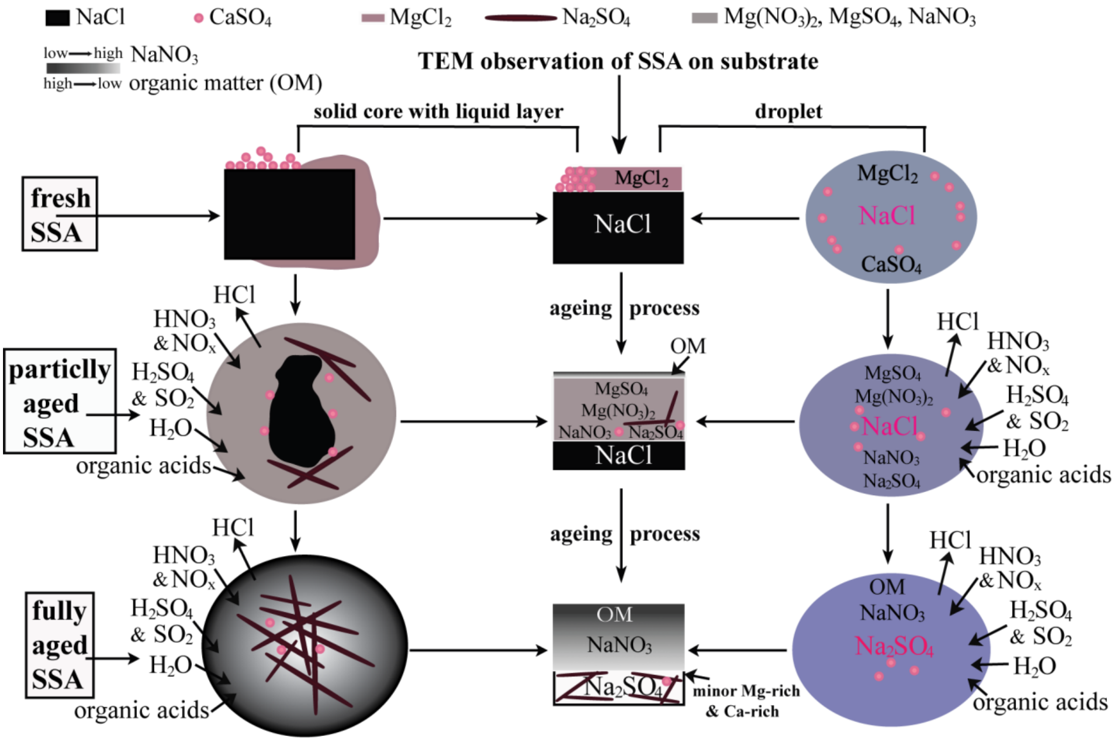

Figure 10. The conceptual model based on our study summarizing the possible SSA ageing processes from fresh, partially aged, and fully aged SSA. Deliquescence RH (DRH) of NaCl is at 75%. SSA ageing could have different processes before and after the DRH.