

Reply to the comments of Anonymous Referees

We thank the reviewers very much for the careful evaluation and valuable comments for our work. We revised the manuscript as much as possible respecting the reviewers' comments.

Specific comments from Anonymous Referee #1 (comments are in italic)

Major Points

- 1. There are a couple key, but specialised terms in this manuscript that have not been defined clearly, making it difficult for a non expert to follow. I suggest explicitly defining eutonic composition and mutual DRH/ERH.*

Response: Thanks for the suggestion. Thermodynamic principles predict that stepwise phase transitions generally occur for two-component solid salt mixtures that can dissolve during the humidification process (Wexler, A. S. and Seinfeld, J. H.: Second-generation inorganic aerosol model, Atmos. Environ., 27A, 2731–2748, doi:10.1016/0960-1686(91)90203-J, 1991). When the mixing ratios of the two-component are at certain values, e.g. $X_{\text{NaCl}} = 0.38$ (or $X_{\text{NaNO}_3} = 0.62$) in Na(Cl, NO₃) mixture, particles act like a single-salt with single phase transitions at the mutual deliquescence relative humidity (MDRH), where the mixture is considered as eutonic composition.

For particles with other mixing ratios ($X_{\text{NaCl}} > 0.38$ or $X_{\text{NaNO}_3} < 0.62$, termed as NaCl-rich; $X_{\text{NaCl}} < 0.38$ or $X_{\text{NaNO}_3} > 0.62$, termed as NaNO₃-rich), the first transition generally occurs at their MDRH, regardless of their mixing ratios; and the aqueous phase resulting from the partial deliquescence has the eutonic composition. The partially dissolved particles keep absorbing water with further increases in the RH and the residual solid component completely dissolves when the RH reaches their DRH, which depends on the richer salt moiety of the particle. During the dehydration process, the concentration of the richer salt moiety becomes dense and firstly crystallize at their efflorescence RH (ERH), and the aqueous phase of the eutonic composition effloresces at their mutual ERH (MERH) with further decreasing RHs.

A more clear and readable description is provided in the revised version, please refer to line 115-127.

2. *The manuscript is missing a description of AIOMFAC calculations. How did you go from model output to DRH? Were these calculations done for the lab generated aerosol only or also every unique composition of sea spray?*

Response: A description of AIOMFAC calculations is provided in the revised version at line 132-137. These calculations were done for the proxy systems including (Na, Mg)(Cl, NO₃) and Na(Cl, NO₃) systems with various mixing ratios of the components.

3. *Could the authors please add some details about how the ambient aerosol samples were stored before analysis. Is there potential for changes in their chemical composition or morphology between collection and measurement?*

Response: The samples were put into black plastic boxes and sealed with parafilm immediately after the collection and these sealed samples were then stored in a refrigerator before the measurements (this paragraph is added at lines 179-180 in the revised version). We believe that this procedure minimizes the sample particle modification, if any.

4. *Could the authors please comment on the use of nitrate salts but not sulfate salts in their sea spray mimic - in the introduction sulfate was listed as a component of SSA but nitrate was not.*

Response: As shown in the manuscript, the elemental concentration of N, based on our low-Z particle EPMA results, is much higher than that of S (7.9(±2.3)% vs. 0.8(±0.3)%). And the elemental ratio of S and Na in SSAs collected in our samples is similar to that of sea water ratios ([S]/[Na] = 0.06, Haynes, W. M.: CRC Handbook of Chemistry and Physics, 96th Edition, CRC Press, Boca Raton, Florida, 14–18, 2015.), so that the SSAs were considered to contain more nitrate due to the reaction with NO_x/HNO₃ instead of sulfate. In addition, sulfate salts generally have DRHs higher

than 90%, which is not consistent with our hygroscopic observations as well. A more detailed explanation is added in the revised version at line 187 and 274-278.

5. *Could the authors comment on their choice to use the ratio of ions in sea water. Divalent cations are known to be enriched in sea spray aerosol (Jayarathne et al. (2016). Enrichment of Saccharides and Divalent Cations in Sea Spray Aerosol During Two Phytoplankton Blooms. Environ. Sci. Technol., 50(11511–11520). <https://doi.org/10.1021/acs.est.6b02988>)*

Response: Please refer to our low-Z particle EPMA results. The elemental ratio of Na:Mg is around 9, which is also close to the seawater ratio (Haynes, 2015), so that we chose to maintain it. It is true that the divalent cations were observed to be enriched during phytoplankton blooms. However, it might not happen during our sampling. An explanation is added into the revised version at lines 192-194.

Minor Points

1. *Line 115 - 119 - This statement is not clear to me. It probably needs to be broken into 2-3 sentences. Is this the case for all binary salt mixtures or just some?*

Response: As for the statement, please see the response to major point #1. Theoretically, this is the case for all binary inorganic salt mixtures.

2. *Line 242 - what are these exception particles chemical compositions?*

Response: Please refer to the secondary electron image in Fig.2, where particles #2 and #7 are Fe-rich, particle #4 is aluminosilicate, and particles #8 and #14 are aged aluminosilicates. Their chemical compositions were provided in Table S1 in the supporting information.

3. *Line 255 - are there figures for these particles?*

Response: Yes, please refer to Fig. 8 and S6-S11 in the supporting information.

4. *Does see-through mean transparent? Consider making this substitution in the manuscript.*

Response: Yes, and the term was coined when we developed the system and has been used afterwards.

5. *Section 3.2 seems redundant with the methods and the following sections. What is the take away message from this section that is not provided in the later discussion of the specific particle types?*

Response: Section 3.2 is a brief description of the hygroscopic behavior of different types of particles that we observed, including their ranges of DRHs and ERHs. This section is simplified and combined into section 3.1 (red marked in the revised version).

6. *I think for clarity, it would be helpful to give the lab generated SSA (surrogate system) a specific name and use it throughout. It seems like sometimes they are called surrogate systems and sometimes just systems, and it becomes hard to follow if it is the lab proxy or some ambient aerosol that has that composition.*

Response: Thanks for the suggestion of the reviewer. The lab generated SSAs (inorganic surrogate system) in this study are termed as Na(Cl, NO₃) and (Na, Mg)(Cl, NO₃) systems. Please refer to lines 334, 374, 377, 405, 431-432, 476, and 485. The two parts including just “system” are changed as “composition”. Please refer to lines 373 and 407.

7. *Section 3.3 could use an intro sentence that reminds the reader that SSA is a fraction of the ambient aerosol.*

Response: The sentence is added into the revised version at line 280.

8. *Line 301 - 304 & 305 - 309 & 365 - 368 was there evidence of organic in the elemental analysis as well?*

Response: Yes. The C contents, which represents organics, were clearly observed in the elemental analysis. Please refer to lines 271-273, X-ray spectra in Fig. 2, and the X-ray maps in Fig S4 and S5 in the supporting information.

9. *Figure 3 scale bar for optical images? It is hard to tell what is 20 μm in the final panel. The whole field of view?*

Response: More clear scale bars are added both for optical images and SEI.

10. *Fig 4/5 - are the lines just joining the points or do they represent something?*

Response: The lines just join the points for better illustration of the phase transitions of particles.

11. *There are many references to the AIOMFAC calculated DRH, but they are not shown anywhere. Consider tabulating these for the SI.*

Response: The AIOMFAC-calculated DRHs are the results from thermodynamic predictions which are based on a thermodynamic equilibrium model.

12. *The captions for Figures 6 and 7 need to be modified so that the reader can understand what is going on in the figure without having to go back through the main text. For example, the two vertical lines are not defined and the phases are not easy to understand without the definitions for P, S, R, Q & T.*

Response: Thank the reviewer for the suggestion, more clear figure captions are provided in the revised version.

13. *Could the authors please check that all the citations made in the text have an entry in the reference section. I noticed Liu et al. 2011 is missing but did not do a thorough check.*

Response: Thanks very much to the reviewer for the suggestion, all the citations are carefully and thoroughly rechecked.

Specific comments from Anonymous Referee #2 (comments are in italic)

1. *I found that the paper was based on 39 particles collected in one sample. How could we ensure the representative of this sample?*

Response: Our main focus is not the characterization of the samples. Instead, we deeply investigated the hygroscopic behavior of ambient aerosols collected at a coastal site in terms of their chemical compositions.

2. *Line 95, an unnecessary parenthesis appeared in the sentence.*

Response: It's corrected.

3. *Figure 2, all the SSAs are classified as "aged SSA". Did the authors find any nascent SSA in their study?*

Response: Indeed, all the SSAs are more or less aged. The information is added at line 241.

4. *Figures 6&7, the caption is too simple. At least the notations of five phases should be explained in the caption.*

Response: Thank the reviewer for the suggestion. More comprehensive figure captions are provided in the revised version.

5. *Section 3.4, although nonSSA particles is not the main component in this paper, pure description without figure is not convenient for reading. It would be better if the authors could move one representative figure from SI into the text in this section.*

Response: Fig. 8 for an aged aluminosilicate particle mixed with SSA is added in the revised version.

6. *The scale bar in Figure S2 was missing too.*

Response: The scale bars are added.

7. *It is necessary to present SEM images of laboratory-generated (Na, Mg)(Cl, NO₃) mixture particles, maybe in Figure S3.*

Response: SEM images are added.

8. *Figures S6-S12, what did the size in SEM image stand for? Scale bar or diameter?*

Response: The size are diameters. The information is added into the figure captions.

1 **Chemical Composition-Dependent Hygroscopic Behavior of Individual Ambient Aerosol**
2 **Particles Collected at a Coastal Site**

3

4 Li Wu^{1,2,+}, Hyo-Jin Eom^{1,3,+}, Hanjin Yoo^{1,4}, Dhrubajyoti Gupta¹, Hye-Rin Cho¹, Pingqing Fu², and
5 Chul-Un Ro^{1,4,*}

6

7 ¹ Department of Chemistry, Inha University, Incheon 22212, Korea

8 ² Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University,
9 Tianjin 300072, China

10 ³ Air Quality Research Division, National Institute of Environmental Research, Incheon 22689, Korea

11 ⁴ Particle Pollution Management Center, Inha University, Incheon 21999, Korea

12

13 * *Correspondence to* Chul-Un Ro (curo@inha.ac.kr)

14 ⁺ Authors with equal contributions

15

16 **Abstract**

17 This study investigated the hygroscopic behavior of individual ambient aerosol particles
18 collected at a coastal site of Jeju Island, Korea. The particles' size change along with phase transitions
19 during humidification and dehydration processes, and their chemical compositions, were determined
20 by optical microscopy and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-
21 EDX), respectively. Of the 39 particles analyzed, 24 were aged sea-spray aerosols (SSAs) with diverse
22 mixing ratios of Cl⁻ and NO₃⁻.

23 The ambient SSAs exhibited multiple deliquescence and efflorescence transitions that were
24 dominantly influenced by NaCl, NaNO₃, MgCl₂, Mg(NO₃)₂ and organic species covering the surface
25 of the aged SSAs. For Cl-rich SSAs with $X_{(\text{Na}, \text{Mg})\text{Cl}} > 0.4$, although some particles showed very slow
26 water uptake at low RHs = ~30%, two major transitions were observed during the humidification
27 process, firstly at RH = ~63.8%, regardless of their chemical compositions, which is the mutual
28 deliquescence relative humidity (MDRH), and secondly at RH = 67.5–73.5%, depending on their
29 chemical compositions, which are the final DRHs. During the dehydration process, the Cl-rich SSAs
30 showed single-stage efflorescence at RH = 33.0–50.5%, due to simultaneous heterogeneous
31 crystallization of inorganic salts. For Cl-depleted SSAs with $X_{(\text{Na}, \text{Mg})\text{Cl}} < 0.4$, two prompt deliquescence

32 transitions were observed during the humidification process, firstly at MDRH = 63.8 % and secondly
33 at RH = 65.4–72.9%. The mutual deliquescence transition was more distinguishable for Cl-depleted
34 SSAs. During the dehydration process, step-wise transitions were observed at efflorescence RHs (ERHs)
35 = 24.6–46.0% and 17.9–30.5%, depending on their chemical compositions.

36 Additionally, aged mineral particles showed partial or complete phase changes with varying
37 RH due to the presence of SSAs and/or NO₃⁻ species. In contrast, non-reacted mineral and Fe-rich
38 particles maintained their size during the entire hygroscopic process. The mixture particles of organic
39 and ammonium sulfate (AS) exhibited lower deliquescence and efflorescence RHs compared to pure
40 AS salt, highlighting the impact of organic species on the hygroscopic behavior of AS. These findings
41 emphasize the complexity of atmospheric aerosols and the importance of considering their composition
42 and mixing state when modeling their hygroscopic behavior and subsequent atmospheric impacts.

43

44 **1 Introduction**

45 Atmospheric aerosols play a significant role in the global climate by directly scattering or
46 absorbing incoming solar radiation and indirectly serving as cloud condensation nuclei (Haywood and
47 Boucher, 2000; Pandis et al., 1995). The hygroscopicity of ambient aerosol particles, critically
48 depending on their compositions, is of vital importance in understanding their properties, including
49 their effects on aerodynamic performance, cloud-droplet nucleation efficiency, optical properties, and
50 heterogeneous chemical reactivity with atmospheric gas-phase species (Krueger et al., 2003; ten Brink,
51 1998; Wang and Martin, 2007; Wu et al., 2020). However, the study of their hygroscopic behavior is
52 challenging because ambient aerosols typically exist as complex mixtures of several chemical species,
53 even at the individual particle level, due to multiphase interactions (Krieger et al., 2012; Pöschl and
54 Shiraiwa, 2015; Schiffer et al., 2018).

55 Sea-spray aerosols (SSAs) are a significant component comprising 25-60% of atmospheric
56 particulate matter mass (Finlayson-Pitts and Pitts, 2000; Song et al., 2022). Understanding the
57 hygroscopic properties of SSAs is essential for study on aerosol-cloud interactions and global climate
58 (Schill et al., 2015; Zieger et al., 2017), which however, is still defective owing to their complex
59 chemical compositions (Cochran et al., 2017; Meskhidze et al., 2013; Xu et al., 2020). Nascent SSAs
60 are formed when bubbles burst at the sea surface, generating both submicron and supermicron SSAs
61 from film and/or jet drops (Quinn et al., 2015; Wang et al., 2017). The primary inorganic constituents
62 of nascent SSAs are Na⁺, Cl⁻, and Mg²⁺, followed by SO₄²⁻, Ca²⁺, K⁺, and other minor compositions

63 (Seinfeld and Pandis, 2006). Submicron nascent SSAs contain more organic species and fewer
64 inorganic salts than supermicron ones (Ault et al., 2013; Prather et al., 2013; Wang et al., 2015). In
65 pristine marine environments, the organics in SSAs mostly originate from phytoplankton activities in
66 the sea, while in polluted marine environments, non-biodegradable surfactants from anthropogenic
67 waste run-offs to the sea are supposed to be added (Cochran et al., 2016; Forestieri et al., 2016).
68 Reactions of SSAs with various atmospheric species, such as NO_x/HNO_3 , $\text{SO}_2/\text{H}_2\text{SO}_4$, and $\text{CH}_3\text{SO}_3\text{H}$,
69 within minutes to hours of residence in air further increase the complexity of the chemical compositions
70 (Liu et al., 2007; Saul et al., 2006; ten Brink, 1998), leading to partially or fully reacted (or aged) SSAs
71 after Cl depletion (Ault et al., 2014; Gard et al., 1998; Laskin et al., 2012; Pósfai et al., 1995; Wu et al.,
72 2020). The further reactive uptake of N_2O_5 was also reported to be dependent on the chloride to nitrate
73 ratio of the reacted SSAs and their phases (Ryder et al., 2014). In addition, SSAs interact with volatile
74 organic carbons (VOCs), secondary organic aerosols (SOAs), etc., in the marine boundary layer (Su et
75 al., 2022). The presence of primary and secondary organics, biogenic species, sea-salt sulfates (ss-
76 SO_4^{2-}), non-sea-salt sulfates (nss- SO_4^{2-}), etc., adds greater complexity to the interdependence of
77 hygroscopic behavior and heterogeneous reactions in ambient SSAs (Ault et al., 2013; Beardsley et al.,
78 2013; Keene et al., 2007; O'dowd and De Leeuw, 2007; Prather et al., 2013).

79 Many studies have investigated the hygroscopic behavior of both airborne and laboratory-
80 generated SSAs. It is generally accepted that sea-salt-containing particles result in higher hygroscopic
81 factors in supermicron particles (Atkinson et al., 2015; Herich et al., 2009). Some single particle
82 measurements have been reported on ambient fine and coarse mode SSAs that are dominated by
83 inorganic salt species. For example, environmental transmission electron microscopy was used to
84 measure the deliquescence and efflorescence relative humidities (DRHs and ERHs) of NaCl-bearing
85 aerosols, sulfate/chloride containing SSAs, Mg-rich particles, etc., collected from clean and polluted
86 environments (Semeniuk et al., 2007; Wise et al., 2007). It was found that NaCl moiety in
87 sulfate/chloride containing SSAs underwent deliquescence at $\sim 75\%$ RH with the sulfate-bearing phases
88 remaining insoluble, which is similar to the DRH of pure NaCl aerosols, whereas the DRH of the NaCl
89 moiety was lowered in the presence of soluble compositions like NaNO_3 . In a follow-up study, the
90 DRHs and ERHs of laboratory-generated and ambient SSA particles were found to be consistent (Wise
91 et al., 2009). Similar observations for marine aerosols with insoluble sulfate moieties and a highly
92 hygroscopic NaCl-moiety were also reported (Freney et al., 2010). In-situ Raman spectrometry was
93 used to probe the phase transitions of SSA droplets (80–100 μm) nebulized from sea-water, which

94 revealed that $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ solidified at $\text{RH} > 90\%$, followed by crystallizations of NaCl and
95 $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ at $\text{RH} = \sim 55\%$ and $\sim 44\%$, respectively (Xiao et al., 2008). Optical microscopy
96 combined with low-Z particle energy-dispersive electron probe X-ray microanalysis (low-Z particle
97 EPMA) was used to determine 2-D growth factors, phase transition RHs, and chemical compositions
98 in ambient aerosols, including nascent and reacted/aged SSAs (Ahn et al., 2010). However, the
99 relationship between hygroscopic properties and the evolving chemical compositions and mixing states
100 of ambient SSAs remains unclear.

101 Laboratory-generated inorganic salt particles have been utilized as surrogates to understand and
102 parameterize the complex hygroscopic properties of SSAs for climate models. Since NaCl constitutes
103 approximately 80% of nascent SSAs by mass, the hygroscopic behavior of pure NaCl particles has been
104 extensively studied for parameterizing the thermodynamic and optical properties and cloud activation
105 efficiency of ambient SSAs (Niedermeier et al., 2008; Tang et al., 1997). However, the hygroscopic
106 growth factors of ambient or laboratory-generated SSAs are reported to be different from those of pure
107 NaCl, possibly due to the presence of hydrates such as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, organic substances, or other
108 impurities (Ahn et al., 2010; Guo et al., 2019; Kong et al., 2018; Rosati et al., 2021; Schindelholz et al.,
109 2014; Zieger et al., 2017). Consequently, the hygroscopic properties of multicomponent systems such
110 as mixed cation chlorides (Chan et al., 2000; Ge et al., 1996, 1998; Gupta et al., 2015a; Li et al., 2014),
111 sodium salts of mixed anions (Chan et al., 1997; Chang and Lee, 2002; Freney et al., 2010; Gupta et
112 al., 2015b), and other mixture systems such as NaCl-MgSO₄ (Woods et al., 2010), NaCl-CaSO₄ (Freney
113 et al., 2010), NaCl-(NH₄)₂SO₄ (Tobon et al., 2021) are of special relevance, which can serve as
114 surrogates for ambient or reacted SSAs.

115 As discussed in detail elsewhere (Gupta et al., 2015a; Li et al., 2014), thermodynamic principles
116 predict stepwise phase transitions in two-component inorganic solid salt mixtures, such as NaCl-KCl,
117 NaCl-MgCl₂, and NaCl-NaNO₃, that can dissolve during the humidification process (Wexler and
118 Seinfeld, 1991). When the mixing ratio of the two-component is at a certain value, e.g. $X_{\text{NaCl}} = 0.38$ (or
119 $X_{\text{NaNO}_3} = 0.62$) in the NaCl-NaNO₃ mixture, particles act like a single-salt and exhibit a single phase
120 transition at its mutual DRH (MDRH), where the mixture is considered to have a eutonic composition.
121 For particles with other mixing ratios, the first transition generally occurs at their MDRH, regardless
122 of the specific ratios; and the resulting aqueous phase from partial deliquescence also possesses the
123 eutonic composition. As RH further increases, partially dissolved particles continue to absorb water
124 until the remaining solid component fully dissolves at the respective DRH, dependent on the salt moiety

125 richer in concentration. During the dehydration process, as RH decreases, the concentration of the richer
126 salt moiety becomes more concentrated, leading to crystallization at their respective ERH. The aqueous
127 phase of the eutonic composition then effloresces at their mutual ERH (MERH) as RH further decreases.

128 Thermodynamic models, such as the Extended Atmospheric Inorganics Model (E-AIM)
129 (<http://www.aim.env.uea.ac.uk/aim/aim.php>; (Ansari and Pandis, 1999; Carslaw et al., 1995; Clegg et
130 al., 1998b, a; Wexler and Clegg, 2002) and the Aerosol Inorganic-Organic Mixtures Functional groups
131 Activity Coefficients (AIOMFAC) (<http://www.aiomfac.caltech.edu>; Zuend et al., 2008, 2011), can
132 predict MDRHs and DRHs for multicomponent mixture systems. The DRH represents the solubility
133 limit (saturation concentration) of a compound in a solution, defining solid–liquid equilibrium. When
134 a solid compound coexists with a saturated liquid mixture, it has a specific molar ion activity product
135 (IAP) in that solution. The AIOMFAC model calculates IAP as a function of RH using ion activity
136 coefficients, which remains constant regardless of other mixture components. The corresponding RH
137 becomes the DRH when the calculated IAP matches that of saturated solutions. However, as
138 efflorescence is a kinetic or rate-driven process, no general theoretical model can predict the
139 efflorescence of single or multicomponent aerosol particles, and thus the best way is experimental
140 observation (Cohen et al., 1987; Martin et al., 2000). Previous modeling and field studies have
141 attributed the reduction in hygroscopic growth of SSAs to the organic fractions (Ming and Russell,
142 2001; Vaishya et al., 2013; Zhang et al., 2014), whereas recent measurements suggest that organic
143 species have an insignificant influence (Nguyen et al., 2017). Therefore, establishing a systematic
144 correlation between the chemical compositions and hygroscopic behavior of ambient SSAs vis-à-vis
145 the multicomponent inorganic surrogates is a priority towards understanding the hygroscopic properties
146 of ambient SSAs and parametrizing phase changes for model applications.

147 Mineral particles, such as aluminosilicates and calcium carbonate, which are typically non-
148 hygroscopic, can become hygroscopic when they are internally mixed with SSAs or react with gaseous
149 species such as NO_x, SO₂, and organic acids in the presence of water vapor (Li et al., 2014; Tang et al.,
150 2016). In fact, mineral dust and aged SSAs may exist as internal and/or external mixtures in the
151 atmosphere (Geng et al., 2014). For instance, Mg-silicate particle coagulated with SSA partially
152 increased in size only at the SSA region with increasing RH and was covered with an aqueous droplet
153 caused by the complete dissolution of the SSA part in high RH (Semeniuk et al., 2007). Additionally,
154 aluminosilicates coated with sulfur-bearing materials or internally mixed with sea salt particles can
155 absorb water, although the aluminosilicates remained as solid phases (Freney et al., 2010).

156 In this study, we systematically investigated the hygroscopic behavior of ambient aerosols
157 collected on Jeju Island, Korea, together with their chemical compositions in various mixing states on
158 a single particle basis. Especially, the hygroscopic properties and chemical compositions of ambient
159 SSAs were examined and compared with multicomponent inorganic surrogate systems containing Na^+ ,
160 Mg^{2+} , Cl^- , and NO_3^- . The phase transitions were observed by monitoring the 2-D size changes of the
161 particles as a function of RH under optical microscopy and the hygroscopic curves and phase diagrams
162 were derived. To determine the chemical compositions of the individual ambient aerosols and the
163 spatial distribution of elements in the effloresced particles, we used scanning electron
164 microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) and analyzed their X-ray spectra and
165 maps, respectively. Although ambient aerosols are complex in their compositions and hygroscopic
166 properties, the detailed elucidation of their hygroscopic behavior according to chemical compositions
167 of ambient aerosols can contribute to the ongoing efforts to improve our understanding of atmospheric
168 aerosols and their impacts on global climate.

169

170 **2 Experimental Section**

171 **2.1 Samples**

172 **Ambient aerosol particles**

173 Aerosol samples were collected on April 16 and 17, 2012, at the Gosan meteorological site
174 (33.29°N, 126.16°E) located on the west coast of Jeju Island in South Korea (see Fig. 1). Ambient
175 aerosols were loaded on TEM grids (200-mesh Cu coated with Formvar stabilized with carbon, Ted
176 Pella, Inc.) mounted on stages 2 and 3 of a three-stage cascade PM_{10} impactor (Dekati Ltd.) with
177 aerodynamic cut-off diameters of 10–2.5 μm and 2.5–1.0 μm , respectively, at a flow rate of 10 L min^{-1} .
178 Sampling durations for each stage were adjusted to collect an appropriate number of particles without
179 overloading. **The samples were put into black plastic boxes and sealed with parafilm immediately after**
180 **the collection and these sealed samples were then stored in a refrigerator before the measurements.**
181 Stage 2 particles, which were sized between 10–2.5 μm , were used to measure chemical composition
182 and hygroscopic behavior in this study.

183

184 **Laboratory-generated (Na, Mg)(Cl, NO_3) mixture particles**

185 In the previous studies (Gupta et al., 2015a, b; Zhang et al., 2004), aerosols of NaCl , NaNO_3 ,
186 $\text{Mg}(\text{NO}_3)_2$, NaCl-NaNO_3 , and NaCl-MgCl_2 were extensively investigated. As Na^+ , Mg^{2+} , Cl^- , and NO_3^-

187 are major species of the ambient SSAs collected in our samples, based on low-Z particle EPMA results,
188 we measured the hygroscopic behavior of NaCl-MgCl₂-NaNO₃-Mg(NO₃)₂ surrogate system in this
189 work to simulate ambient SSAs that contain similar major elements. Pure solutions (1.0 M each) of
190 NaCl (>99.9% purity, Aldrich), MgCl₂·6H₂O, and NaNO₃ (99.9% purity, Aldrich) were prepared using
191 de-ionized water (18 MΩ, Millipore Direct-QTM). The pure solutions were then mixed to obtain
192 solutions with [Cl⁻]:[NO₃⁻] = 3:1, 1:1, and 1:3 (i.e. $X_{(\text{Na},\text{Mg})\text{Cl}} = 0.75, 0.5, \text{ and } 0.25$), while maintaining
193 the sea water ratio of [Na⁺] : [Mg²⁺] = 9:1 (Haynes, 2015), as the elemental ratio of Na and Mg in the
194 ambient SSAs from our samples is also approximately 9. A single jet atomizer (HCT4810) was used to
195 generate aerosol particles from the mixture solutions on hydrophobic TEM grids. Herein, a notation
196 system is used to represent aerosol particles of NaCl-MgCl₂-NaNO₃-Mg(NO₃)₂ as (Na, Mg)(Cl, NO₃).

197

198 2.2 Hygroscopic property measurements

199 The experimental setup for measuring hygroscopic behavior consists of three main components:
200 (A) a see-through impactor, (B) an optical microscope, and (C) a humidity control system. The TEM
201 grid with aerosol particles was attached to the impaction plate in the see-through impactor, and the RH
202 was controlled by mixing dry and wet gaseous N₂ (99.999% purity) flows that were adjusted to obtain
203 the desired RH in the range of ~5.0–92.0%. The humidity control system used wet N₂ gas obtained by
204 bubbling through deionized water reservoirs. The RH was monitored by a digital hygrometer (Testo
205 645) that was calibrated using a dew-point hygrometer (M2 Plus-RH, GE) to provide RH readings with
206 ±0.5% reproducibility. A detailed discussion of the impactor and humidity-controlling system can be
207 found elsewhere (Li et al., 2021). The particles were continuously imaged in RH = 1% steps using a
208 digital camera (Canon EOS 5D, full frame, Canon EF f/3.5 L macro USM lens) mounted on an optical
209 microscope (Olympus, BX51M) during the humidification process (by increasing RH from ~5.0 to
210 92.0 %), followed by the dehydration process (by decreasing RH from ~92.0 to 5.0 %). The changes in
211 particle size with the variation of RH were monitored by measuring the particle areas in the optical
212 images to generate hygroscopic curves. Each humidity condition was sustained for at least 2 mins to
213 allow for sufficient time for water condensation or evaporation. The hygroscopic curves are represented
214 by the area ratio (A/A_0) as a function of RH, where the 2-D projected aerosol area at a given RH (A) is
215 divided by that before starting the humidification process (A_0). The images were processed using image
216 analysis software (Matrox, Inspector v9.0). The experiments were conducted at room temperature ($T =$

217 22 ± 1 °C). Pure NaCl particles were used to verify the accuracy of the system with DRH = 75.5 (±
218 0.5) % and ERH = 46.3–47.6 %.

219

220 **2.3 Low-Z particle EPMA measurements using SEM-EDX**

221 The ambient aerosol particles were analyzed using low-Z particle EPMA measurements with a
222 Jeol JSM-6390 SEM equipped with an Oxford Link super atmospheric thin window (SATW) EDX
223 detector. The analysis was conducted both before and after the hygroscopic processes to find out fields
224 on TEM grids with well-separated particles based on their secondary electron images (SEIs, ~ 100 μm
225 x 100 μm for a field) and to determine the morphology, chemical composition, and spatial distribution
226 of the chemical elements (elemental maps), respectively. The resolution of the detector was 133 eV for
227 Mn Kα X-rays. Point mode and area mode X-ray spectra and elemental maps of individual particles
228 were recorded using Oxford INCA Energy software. An accelerating voltage of 10 kV and beam current
229 of 0.5 nA were used, and typical measurement durations were 20 sec. for point mode, 1 min. for area
230 mode, and 5-10 min. for elemental mapping.

231 The AXIL program was used to obtain the net X-ray intensities for chemical elements through
232 non-linear least-squares fitting of the spectra. From these intensities, the elemental concentrations of
233 individual particles were determined (Vekemans et al., 1994). For individual particles sitting on TEM
234 grids, C and O concentrations were determined using a Monte Carlo calculation technique to correct
235 for the interfering X-ray peaks of C and O emitted from the TEM grid, providing accurate quantification
236 results (Geng et al., 2010). A detailed explanation of the elemental quantification procedure can be
237 found elsewhere (Wu et al., 2019).

238

239 **3 Results and Discussion**

240 **3.1 Chemical composition and hygroscopic behavior of individual ambient aerosol particles**

241 In this study, a total of 39 particles on three fields were investigated, including 24 aged/reacted
242 SSAs with diverse mixing ratios of Cl⁻ and NO₃⁻ and 15 other particles such as six aluminosilicates,
243 five Ca-containing particles, two Fe-rich particles, an aged SiO₂, and a mixture particle of organic and
244 (NH₄)₂SO₄. The mole fraction of Cl as $X_{(Na,Mg)Cl}$ in the aged/reacted SSAs was calculated based on
245 $[Cl^-]/([Na^+]+2[Mg^{2+}])$ to determine the degree of Cl-depletion in the SSA particles. Fig. 2 shows the
246 SEI of the first field containing 16 particles, where the chemical species of each particle are indicated,
247 together with two exemplar X-ray spectra of aged SSAs #5 and #11 with $X_{(Na,Mg)Cl} = 0.75$ and 0.23,

248 respectively. The elemental concentrations of all particles and their chemical species, determined by X-
249 ray spectral analysis, are listed in Table S1 of Supporting Information.

250 In Fig. 3, optical images obtained at different RHs during the humidification and dehydration
251 processes and the secondary electron image (SEIs) after hygroscopic process for 16 particles on the
252 first field are shown. Except particles #2, #4, #7, #8, and #14, the rest are aged SSAs. Optical images
253 and the SEIs for particles on the second and third fields are provided in Figs. S1 and S2, respectively.
254 Particles were initially solid at RH = 5.3 % before the hygroscopic measurement, as shown in Fig. 3A.
255 During the humidification process, most of the SSAs showed partial deliquescence at RH = 63.8 %
256 (Fig. 3C), regardless of their aging degree, indicating the realization of the MDRH. Upon further
257 increase of RH, SSAs underwent full deliquescence transitions at DRH = 65.4 – 73.5 %, which varied
258 for each SSA, as shown in Figs. 3D and E. During the dehydration process, almost all SSAs exhibited
259 colored ring-type patterns (Figs. 3G and H) due to the diffraction of visible light typically observed in
260 the presence of organic surfactants on water, indicating the presence of considerable amounts of organic
261 species in aged SSAs. SSA droplet #5 crystallized at ERH = 50.5 % (Fig. 3G), while the others
262 effloresced over a lower range of ERH = 46.0 – 17.9%. The various DRHs and ERHs indicate different
263 chemical compositions of SSAs.

264 Aluminosilicates and Fe-rich particles did not exhibit any water uptake or changes as a function
265 of RH. Aged aluminosilicates, aged SiO₂, and some reacted Ca-containing particles showed modest
266 growth/shrinkage continuously due to the presence of amorphous NO₃⁻ phases (Ahn et al., 2010). The
267 mixture particle of organic and ammonium sulfate experienced distinct deliquescence and efflorescence.
268 Detailed description of hygroscopic behavior of the ambient aerosol particles is given as follows.

269

270 3.2 SSA particles

271 The average atomic concentrations of C, Na, Cl, N, Mg, S, K, and Ca in SSAs are listed in Table
272 S1 with the values being 43.0(±7.2)%, 13.6(±4.6)%, 8.0(±6.6)%, 7.9(±2.3)%, 1.5(±0.4)%, 0.8(±0.3)%,
273 0.3(±0.1)%, and 0.3(±0.1)%, respectively. The elemental analysis of the SSAs indicates that they
274 consist primarily of Na⁺, Mg²⁺, Cl⁻, NO₃⁻, and organic species. The elemental concentration of N is
275 significantly higher than that of S, and the elemental ratio of S and Na in the ambient SSAs collected
276 from our samples closely resembles that of sea water ([S]/[Na] = 0.06; Haynes, 2015). As a result, the
277 SSAs is considered to contain more nitrate due to the rapid reaction with NO_x/HNO₃, as opposed to
278 sulfate. As the SSAs become more aged or reacted, their mole fractions of Cl⁻ relative to Na⁺ and Mg²⁺

279 decrease, while their mole fractions of NO_3^- increase. Although the aged/reacted SSAs are a
280 complicated multi-component system as a fraction of ambient aerosols, $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ mixture
281 system is considered as an inorganic surrogate system for understanding their hygroscopic behavior.
282 The AIOMFAC model predicts the eutonic compositions of $\text{Na}(\text{Cl}, \text{NO}_3)$ and $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$
283 mixture systems as $X_{\text{NaCl}} = 0.38$ and $X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.46$, respectively. The mole fraction of Cl in the
284 eutonic compositions of the inorganic component of the aged SSAs would be around 0.4. And thus, the
285 SSAs can be classified as Cl-rich or Cl-depleted depending on their $X_{(\text{Na}, \text{Mg})\text{Cl}}$ values being greater or
286 less than 0.4, respectively.

287

288 3.2.1 Cl-rich SSAs

289 Fig. 4 displays the projected 2-dimensional (2-D) area ratio and optical images for Cl-rich SSAs
290 #5 and #19 (panels a and d, respectively), and the 2-D area ratio of humidification (panels b and e) and
291 dehydration (panels c and f) for the two SSAs as a function of RH. For SSAs #5 and #19 the mole
292 fraction of chloride, $X_{(\text{Na}, \text{Mg})\text{Cl}}$ was calculated to be 0.75 and 0.72, respectively. In addition, the figure
293 also includes the $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ particle with $X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.75$ for comparison.

294 During the humidification process, SSAs #5 and #19 initially remained constant in size until
295 RH reached around 30%, after which they gradually increased in size. This behavior is also consistent
296 with the $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ system (Figs. 4b and e), suggesting that $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (DRH = 33.3 %) or
297 Mg^{2+} -rich eutonic part may have undergone water absorption (Gupta et al., 2015a; Zieger et al., 2017).
298 However, the deliquescence transitions were not as distinct as those in particles with $X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.25$
299 and 0.5 generated from $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ mixture solutions (see Fig. S3 in the Supporting Information).
300 The size increase was followed by a shrinkage until RH = 60.5% due to structural rearrangement in the
301 remaining undissolved salt-mixture crystals. Structural rearrangements are commonly observed after
302 preliminary absorption of water at RHs just before the prompt deliquescence transition (Ahn et al.,
303 2010; Gupta et al., 2015a,b; Mikhailov et al., 2009). At first DRH = 63.8%, a partial droplet-like shape
304 appeared in the particle morphology although there was no significant change in the 2-D area ratio.
305 Clear final deliquescence transitions were observed in both SSAs #5 and #19 at DRHs = 73.5 % and
306 72.9 %, respectively, due to the dissolution of the remaining solid NaCl moiety in these Cl-rich particles.
307 The measured DRHs of SSAs #5 and #19 were closer to the final DRHs calculated for the $\text{Na}(\text{Cl}, \text{NO}_3)$
308 system using the AIOMFAC model (Fig. 6), and higher than the calculated and measured ones in the
309 $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ particles (Figs. 4b and e and Fig. 6). These observations for the Cl-rich SSAs suggest

310 that most of the Mg^{2+} salts ($MgCl_2 \cdot 6H_2O$ with DRH = 33.3 %; $Mg(NO_3)_2$ with DRH = 52%) have
311 already dissolved at low RHs or undergone complexation with organic moieties (Eom et al., 2016), and
312 the remaining NaCl and $NaNO_3$ moieties drove the deliquescence transition. The hygroscopic growth
313 of both SSAs #5 and #19 was much smaller than that of the (Na, Mg)(Cl, NO_3) system (Figs. 4b and e)
314 when RH was raised to 91.4%, indicating the presence of a partitioning hydrophobic layer composed
315 of organic surfactants that covered the aqueous salt droplets and inhibited water uptake (Bertram et al.,
316 2018; Cochran et al., 2016; Eom et al., 2016; Lee et al., 2020).

317 During the dehydration process as RH decreased from ~91% to ~5%, both the SSA droplets
318 showed a continuous shrinkage in size before their efflorescence. However, the rate of shrinkage was
319 much smaller than that of pure inorganic surrogates, such as the (Na, Mg)(Cl, NO_3) system with
320 $X_{(Na,Mg)Cl} = 0.75$ (Figs. 4c and f), indicating that the hydrophobic surfactant layers covering the aqueous
321 salt droplets potentially impeded the water evaporation. SSAs #5 and #19 showed one clear
322 efflorescence transition at RH = 50.5% and 45.0%, respectively (Figs. 4a and d). Interestingly, SSA #5
323 ($X_{(Na,Mg)Cl} = 0.75$) underwent a sharp decrease in size from RH = 50.9 – 50.5%, which is considerably
324 higher than the ERH range of ~45 – 47% for pure NaCl particles (Ahn et al., 2010; Eom et al., 2014;
325 Martin, 2000), and the first ERHs of either Na(Cl, NO_3) (Fig. 7) or (Na, Mg)(Cl, NO_3) (Figs. 4c and 7)
326 systems. On the other hand, SSA #19 ($X_{(Na,Mg)Cl} = 0.72$) first showed a small decrease in size at RH =
327 63.8 – 60.8%, which is not a typical efflorescence transition, followed by a sharp decrease in size at
328 RH = 45.8 – 45.0%, which is on the lower side of the ERH range for pure NaCl and slightly higher
329 than the first ERHs of Na(Cl, NO_3) and (Na, Mg)(Cl, NO_3) systems (Figs. 4f and 7). The higher ERH
330 at RH = 50.5 % in SSA #5 indicates heterogeneous efflorescence of the NaCl moiety, while the ERH =
331 45.0% in SSA #19 suggests the homogeneous nucleation of NaCl moiety. Both SSA droplets showed
332 just one decisive efflorescence transition at their ERHs, indicating co-crystallization of most aqueous
333 inorganic salt moieties along with NaCl, pointing towards the likelihood that the SSAs with more
334 complicated chemical compositions than the (Na, Mg)(Cl, NO_3) mixture aerosols contain chemicals
335 which can act as seeds, such as (Na, Ca) SO_4 crystals, for the complete crystallization at the
336 efflorescence transition. These observations are substantiated by the distribution of S and O at the center
337 and edge of the NaCl moiety in the X-ray maps obtained from the effloresced SSA particles #5 and #19,
338 respectively (Fig. S4) (Li et al., 2014; Gupta et al., 2015a). The apparent (not so sharp) decrease in size
339 of SSA #19 at RH = 63.8 – 60.8% could be attributed to: (i) the sudden shrinkage of viscous organic
340 moieties covering the aqueous salt droplet; or (ii) inhibited or slow water loss, probably due to a kinetic

341 barrier to crystallization from amorphous/gel forming moieties such as
342 $\text{MgSO}_4/\text{Mg}(\text{NO}_3)_2/(\text{CH}_3\text{SO}_3)_2(\text{Mg}, \text{Ca})$ (Liu and Laskin, 2009; Xiao et al., 2008; Zhang et al., 2004;
343 Zhao et al., 2006); or (iii) a phase transition, such as heterogeneous efflorescence, had occurred, but
344 the presence of viscous moieties (organics or Mg^{2+} - organic complex) affected the relative 2-D size
345 decrease on the TEM grid substrate.

346

347 3.2.2 Equimolar and Cl-depleted SSAs

348 Fig. 5 shows the plots of the projected 2-D area ratio and optical images for an equimolar SSA
349 #23 (Fig. 5a) and a Cl-depleted SSA #11 (Fig. 5d), and 2-D area ratio of humidification (panels b and
350 e) and dehydration (panels c and f) for the two SSAs as a function of RH. The calculated mole fractions
351 of chloride, $X_{(\text{Na}, \text{Mg})\text{Cl}}$ for SSAs #23 and #11 are 0.52 and 0.23, respectively. The figure also includes
352 the $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ particles with $X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.5$ and 0.25 for comparison.

353 During the humidification process, both SSAs #23 and #11 remained relatively constant until
354 $\text{RH} = \sim 50\%$, unlike the $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ system, probably due to the decreased concentration of
355 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The particle size then began to shrink until $\text{RH} = \sim 59\%$. Both SSAs exhibited two distinct
356 deliquescence transitions. Partial deliquescence transitions occurred at $\text{RH} = \sim 63.8\%$, which is the
357 MDRH for the mixture of soluble moieties in the ambient SSAs and was reported for the first time.
358 Both SSAs exhibited two clear deliquescence transitions. The observed and AIOMFAC-calculated
359 MDRHs of the $\text{Na}(\text{Cl}, \text{NO}_3)$ system are $\sim 68\%$, while the AIOMFAC-calculated second MDRH for the
360 $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ system is 66.5% after the dissolution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at the calculated first MDRH
361 of $\sim 34\%$, as shown in Fig. 6. This indicates that the eutonic component in the ambient SSAs, with a
362 lower MDRH of 63.8%, is composed of NaCl , NaNO_3 , $\text{Mg}(\text{NO}_3)_2$, and some other minor, less-soluble
363 moieties. The mutual deliquescence transition was more distinct in Cl-depleted SSAs than in Cl-rich
364 SSAs, suggesting that the eutonic component in the ambient SSAs is richer with other salts compared
365 to NaCl . As RH increased further, both SSAs #23 and #11 underwent final deliquescence transitions at
366 DRHs = 69.5%. The observed DRH for SSA #23 ($X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.52$) is closer to the final DRH calculated
367 from AIOMFAC for pure NaCl moiety in the $\text{Na}(\text{Cl}, \text{NO}_3)$ system (Fig. 6), and higher than the
368 AIOMFAC-calculated final DRH for pure NaCl moiety in the $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ system (Figs. 5b and
369 6). The observed DRH for SSA #11 ($X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.23$) is lower than the AIOMFAC-calculated final
370 DRH (Fig. 6) for pure NaNO_3 moiety in the $\text{Na}(\text{Cl}, \text{NO}_3)$ system (Gupta et al., 2015b), and close to the
371 AIOMFAC-calculated final DRH for pure NaNO_3 moiety in the $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ system (Figs. 5e

372 and 6). The observation of Cl-depleted SSAs during humidification suggests that a (Na, Mg)(Cl, NO₃)
373 dominant **composition** drives the deliquescence transition. As RH increased further, the hygroscopic
374 growth of both SSAs #23 and #11 was stunted, in comparison to the **(Na, Mg)(Cl, NO₃) mixture systems**
375 (Figs. 5b and e), likely due to the presence of hydrophobic surfactants covering the aqueous salt droplet.

376 During the dehydration process, both SSAs #23 and #11 showed slower rates of shrinkage
377 compared to the **(Na, Mg)(Cl, NO₃) mixture systems** (Figs. 5c and f), suggesting inhibition of water
378 evaporation due to surface hydrophobic organic moieties. The diffraction patterns at the aqueous salt
379 droplet-organic surfactant interface were more prominent in the form of color and/or ring-like patterns
380 for equimolar and Cl-depleted SSAs (Figs. 5a and d), indicating that the hydrophobic organic film may
381 become thicker, or the concentration of organic surfactants may increase with aging. During
382 dehydration, SSA #23, which is equimolar or slightly Cl-rich, showed one sharp transition at RH =
383 44.1–43.6% and a gradual decrease in size thereafter until RH = 30.7%, which is not considered an
384 efflorescence transition (Fig. 5a). The distinct ERH of 43.6% observed for SSA #23 was higher than
385 the first ERHs of both Na(Cl, NO₃) and (Na, Mg)(Cl, NO₃) systems (Fig. 5c and 7), indicating possible
386 homogeneous efflorescence of NaCl along with other salts on crystalline seeds such as (Ca, Na)SO₄
387 (Pósfai et al., 1995; Semeniuk et al., 2007; Wise et al., 2007), as shown in the X-ray maps in Fig. S5a.
388 The remaining metastable amorphous/gel type NO₃⁻ moieties and MgSO₄·xH₂O may be responsible
389 for the gradual decrease in size after the efflorescence transition (Li et al., 2016). Cl-depleted SSA #11
390 showed two clear efflorescence transitions at RH = 44.1–39.6% and 24.6–23.9%, as shown in Fig. 5d.
391 The first ERH of 39.6% measured for SSA #11 was also higher than the ERHs for both Na(Cl, NO₃)
392 and (Na, Mg)(Cl, NO₃) systems, while the second ERH of 23.9% was close to and lower than the ERH
393 range for pure NaCl in (Na, Mg)(Cl, NO₃) and Na(Cl, NO₃) systems, respectively (Figs. 5f and 7). The
394 observations for Cl-depleted SSA #11 suggest that the first ERH was most probably due to the
395 heterogeneous crystallization of the dominant NaNO₃ and/or Mg(NO₃)₂ on mixed cation sulfate
396 crystalline seeds such as (Ca, Na)SO₄, while NaCl continued to homogeneously nucleate until the
397 second ERH, where it crystallized at the center/core of the particle (Woods et al., 2013), as shown in
398 the X-ray maps in Fig. S5b.

399
400 **3.2.3 Phase diagrams of ambient SSAs in correlation with Na(Cl, NO₃) and (Na, Mg)(Cl, NO₃)**
401 **surrogates systems**

402 The phase diagrams of ambient SSAs in correlation with Na(Cl, NO₃) and (Na, Mg)(Cl, NO₃)
403 surrogate systems can show the relationship between the observed deliquescence and efflorescence
404 behavior of the ambient SSAs and those of the two surrogate systems. The ambient SSAs have more
405 complex compositions, but the simpler Na(Cl, NO₃) and (Na, Mg)(Cl, NO₃) surrogate systems can help
406 to identify the dominant salts and their behavior in the ambient SSAs. For example, the observation of
407 Cl-depleted SSAs during humidification suggests that a (Na, Mg)(Cl, NO₃) dominant composition
408 drives the deliquescence transition. This information can be useful in understanding the hygroscopic
409 properties and behavior of atmospheric aerosols.

410

411 3.2.3.1 Deliquescence phase diagram

412 Fig. 6 shows the experimentally measured DRHs for the ambient SSA particles and those of the
413 (Na, Mg)(Cl, NO₃) and Na(Cl, NO₃) systems, calculated from the AIOMFAC model, plotted as a
414 function of the mole fraction of chloride, $f(X_{(\text{Na, Mg})\text{Cl}}$ or X_{NaCl}).

415 The first MDRH of the (Na, Mg)(Cl, NO₃) system, which was calculated from AIOMFAC, is
416 34.2%, and the MDRH measured in laboratory-generated (Na, Mg)(Cl, NO₃) particles is ~33.4% (Fig.
417 S3). These values are attributed to the dominant MgCl₂·6H₂O eutonic component (Gupta et al., 2015a).
418 In some Cl-rich SSAs, a gradual increase in size and a change in morphology were observed at RH =
419 ~33%, indicating that they were in the partial aqueous phase (Figs. 4a and d). It is also possible that the
420 gradual water uptake observed in SSAs at low RHs is due to amorphous inorganic moieties such as
421 MgSO₄·xH₂O (Xiao et al., 2008; Zhao et al., 2006) and Mg(NO₃)₂·xH₂O (Zhang et al., 2004), and/or
422 water-soluble secondary organics such as carboxylate salts formed due to reactions of the (Na, Mg)Cl
423 species with dicarboxylic acids, which are ubiquitous in the marine boundary layer (Ghorai et al., 2014;
424 Laskin et al., 2012; Li et al., 2021). Wise et al. (2009) reported that ambient SSAs started changing in
425 morphology at 36(±15)% RH.

426 For the (Na, Mg)(Cl, NO₃) system, the eutonic composition is $X_{(\text{Na, Mg})\text{Cl}} = 0.46$, with a second
427 MDRH of 66.5%, calculated from AIOMFAC, and a measured value of ~66.6(±0.4)% in the laboratory-
428 generated (Na, Mg)(Cl, NO₃) particles (Fig. S3). For the Na(Cl, NO₃) system, the eutonic composition
429 is $X_{\text{NaCl}} = 0.38$, with the MDRH of 67.9%, calculated from AIOMFAC, and a measured value of
430 ~67.9(±0.3)% in the laboratory-generated particles (Gupta et al., 2015b). The observed MDRH of
431 63.8(±0.3)% for the ambient SSAs (Fig. 6) is slightly lower than those of the Na(Cl, NO₃) and (Na,
432 Mg)(Cl, NO₃) mixture systems, indicating that the eutonic component in the mutual deliquescence

433 transition may be Na(Cl, NO₃)-rich, with minor concentrations of other soluble salt moieties, as the
434 MDRH of salt mixtures is generally lower than individual salt DRHs (Wexler and Seinfeld, 1991). It is
435 less likely that Na₂SO₄ or CH₃SO₃Na are major components of the eutonic component in these ambient
436 SSAs, as they have much higher MDRHs, i.e., MDRHs = 84.0% for Na(Cl, SO₄) and 71% for Na(Cl,
437 CH₃SO₃) (Chang and Lee, 2002; Liu and Laskin, 2009; Liu et al., 2011). The lowest final DRH
438 measured for SSA #1 with $X_{(\text{Na},\text{Mg})\text{Cl}} = 0.33$ is at RH = 65.4 % (Fig. 6), which is close to the observed
439 MDRH of 63.8(±0.3)%, suggesting that the eutonic component likely has a chloride mole fraction
440 within the range of $X_{(\text{Na},\text{Mg})\text{Cl}} = \sim 0.30\text{--}0.40$. Interestingly, Wise et al. (2009) reported rounding in
441 particle morphology at RH = 65(±4)%, which is close to the observed MDRH but was not confirmed
442 as such since only four ambient SSA particles were studied.

443 The final DRHs in both (Na, Mg)(Cl, NO₃) and Na(Cl, NO₃) systems are solely determined by
444 the solid salt remaining after the mutual deliquescence of the eutonic component. Fig. 6 clearly shows
445 that for the Cl-rich SSA particles with $X_{(\text{Na},\text{Mg})\text{Cl}} > 0.40$, which contain more NaCl than the eutonic
446 composition, the final DRH values (~67.5-73.5%) approached the DRH of pure NaCl salt (~75.3% at
447 298 K) as the chloride concentration increased. Similarly, for the Cl-depleted particles with $X_{(\text{Na},\text{Mg})\text{Cl}} <$
448 0.40, the final DRH values (~65.4-72.9%) approached that of pure NaNO₃ salt (~74% at 298 K) as the
449 chloride concentration decreased.

450 The chemical components of each phase in the ambient SSAs during the humidification process
451 are not well known, therefore, five possible single and/or mixed phases are notated as alphabets (P, Q,
452 R, S, and T) and the possible major chemical components in each phase (s = solid; aq = aqueous) are
453 listed as follows:

- 454 (i) P-(s): all components are mixed in solid phase at RH < ~33–35% at all mole fractions of chloride.
455 (ii) Q-(s + aq): a mixed phase comprising possibly aqueous MgCl₂·6H₂O dominant eutonic
456 components + solid NaCl, (Na, Mg, Ca)(NO₃, SO₄) and organics between RH = ~33% and the
457 first clear MDRH of ~63.8%.
458 (iii) R-(s + aq): a mixed phase comprising solid NaNO₃ and (Ca, Na)SO₄ + aqueous eutonic
459 components rich in Na(Cl, NO₃) and Mg(NO₃, SO₄, organics) between RH = 63.8% and final
460 DRHs for $X_{(\text{Na},\text{Mg})\text{Cl}} < 0.40$, i.e., Cl-depleted SSAs.
461 (iv) S-(s + aq): a mixed phase comprising solid NaCl and (Ca, Na)SO₄ + aqueous eutonic
462 components rich in Na(Cl, NO₃) and Mg(Cl, NO₃, SO₄, organics) between the RH = 63.8% and

463 final DRHs for $X_{(\text{Na},\text{Mg})\text{Cl}} > 0.40$, i.e., Cl-rich SSAs.

464 (v) T-(aq): aqueous phase for most components including NaCl, NaNO₃, and Mg(Cl, NO₃, SO₄,
465 organics) above the measured final DRHs at all mole fractions of chloride, while (Ca, Na)SO₄
466 should remain in crystalline solid phase and does not take part in the deliquescence transitions
467 in the measured RH range.

468

469 3.2.3.2 Efflorescence phase diagram

470 The experimentally measured ERHs for the ambient SSA particles and those of (Na, Mg)(Cl,
471 NO₃) and Na(Cl, NO₃) systems are plotted as a function of the mole fraction of chloride, $f(X_{(\text{Na},\text{Mg})\text{Cl}}$ or
472 X_{NaCl}) in Fig. 7.

473 The first ERH values decrease from 44.5% to 24.8% and from 47.1% to 20.2% with decreasing
474 mole fractions of chloride for $X_{(\text{Na},\text{Mg})\text{Cl}} = 0.75$ to 0.25 in the (Na, Mg)(Cl, NO₃) and $X_{\text{NaCl}} = 0.9$ to 0.1
475 in the Na(Cl, NO₃) systems, respectively (Gupta et al., 2015b; Woods et al., 2013). This suggests that
476 the first efflorescence transitions in the Na(Cl, NO₃) and (Na, Mg)(Cl, NO₃) mixture systems are solely
477 due to the homogeneous nucleation of NaCl for both Cl-rich and Cl-depleted particles, and that the
478 amorphous (Na, Mg)NO₃ species cannot undergo homogeneous crystallization even at high
479 supersaturation (Kim et al., 2012; Zhang et al., 2004). In the case of Cl-rich ($X_{(\text{Na},\text{Mg})\text{Cl}} > 0.40$) ambient
480 SSAs, the first ERHs systematically decreased ranging from 50.5% to 33.0% due to the homogeneous
481 nucleation of NaCl for most particles. However, for a few particles, such as SSA #5 (Fig. 4a, ERH =
482 50.5%), NaCl underwent heterogeneous crystallization on the mixed cation sulfate (Ca, Na)SO₄
483 crystalline seeds, resulting in higher ERH values. On the other hand, in Cl-depleted ($X_{(\text{Na},\text{Mg})\text{Cl}} < 0.40$)
484 SSA particles, the first ERH values ranged from 46.0% to 24.6% as a random set of values higher than
485 the first ERHs in Na(Cl, NO₃) and (Na, Mg)(Cl, NO₃) mixture systems (Fig. 7), indicating
486 heterogeneous crystallization of the richer (Na, Mg)NO₃ moieties on the mixed cation sulfate
487 crystalline seeds for most particles.

488 The second/final ERH in the Na(Cl, NO₃) system was only observed for Cl-rich particles (X_{NaCl}
489 > 0.38) due to the mutual efflorescence of the eutonic component ($X_{\text{NaCl}} = 0.38$) at MERH =
490 ~ 30.0 – 35.5% , while no second ERH was recorded for Cl-depleted particles as NaNO₃ heterogeneously
491 crystallized simultaneously on the homogeneously nucleated NaCl seeds (Gupta et al., 2015a). For the
492 (Na, Mg)(Cl, NO₃), a second ERH = ~ 29.6 – 27.4% was only observed for $X_{(\text{Na},\text{Mg})\text{Cl}} = 0.5$ among the

493 three compositions measured (Fig. S3), probably due to the stochastic heterogeneous crystallization of
494 the Na(Cl, NO₃)-rich eutonic moiety on the NaCl seed. On the other hand, the typical transitions from
495 30.5% to 17.9% for the second/final ERH in ambient SSAs were only observed for Cl-depleted particles
496 with decreasing chloride concentration, i.e. $X_{(\text{Na}, \text{Mg})\text{Cl}} = \sim 0.33$ to 0.15, indicating homogeneous
497 nucleation of NaCl followed by assumed simultaneous heterogeneous crystallization of remaining
498 aqueous salt moieties such as Mg(SO₄, NO₃).

499 In the laboratory-generated (Na, Mg)(Cl, NO₃) particles with different mole fractions of
500 chloride, i.e. $X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.25, 0.5, 0.75$ (Fig. S3), and 1.0 (Gupta et al., 2015a), clear final ERHs or
501 MERHs were observed at low RHs ranging in 11.0–5.1% ($X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.25, 0.5$, and 1.0) and 14.6–12.1%
502 ($X_{(\text{Na}, \text{Mg})\text{Cl}} = 0.75$), probably due to the crystallization of the dominant eutonic component of
503 MgCl₂·4H₂O and MgCl₂·6H₂O, respectively. However, such low values of ERHs were not observed in
504 the ambient SSAs, possibly because the concentrations of MgCl₂·xH₂O were too small to be detected
505 by the optical microscopy-derived 2-D area ratio. On the other hand, the very gradual shrinkage
506 observed in ambient SSAs at low RHs may be due to the presence of amorphous Mg(NO₃, SO₄)·xH₂O
507 moieties, which were present in some particles (e.g., SSAs #5, #19, and #23 in Figs. 4a, 4d, and 5a).

508 Considering the possibility of water content at low RHs during the dehydration process (Cziczo
509 et al., 1997; Gupta et al., 2015a; Tang et al., 1997), the ambient SSAs can be divided into five potential
510 phases, denoted as alphabets (P, Q, R, S, T), based on the presence of different chemical components
511 and their states at different relative humidities (RHs) and the major chemical components in each phase
512 (s = solid; aq = aqueous) are listed as follows:

- 513 (i) P-(aq): Almost all components, including NaCl, NaNO₃, and Mg(Cl, NO₃, SO₄, organics), are
514 mixed in the aqueous phase at RH > ~55% for all mole fractions of chloride. The (Ca, Na)SO₄
515 should remain in the crystalline solid phase as it does not take part in the phase transitions within
516 the measured RH range.
- 517 (ii) Q-(s + aq): a mixed phase including solid NaCl and other heterogeneously crystallized moieties
518 + aqueous nucleating species like (Mg·xH₂O)²⁺ and Cl⁻/NO₃⁻/SO₄²⁻ at RHs < 50.5% in Cl-rich
519 SSAs ($X_{(\text{Na}, \text{Mg})\text{Cl}} > 0.40$).
- 520 (iii) R-(s + aq): a mixed phase including heterogeneously crystallized (Na, Mg)NO₃·xH₂O on
521 crystalline (Ca, Na)SO₄(xH₂O) seeds + aqueous NaCl and other moieties, between the first
522 ERHs = 46.0–24.6% and final ERHs = 30.5–17.9% for Cl-depleted SSAs ($X_{(\text{Na}, \text{Mg})\text{Cl}} < 0.40$).

523 (iv) S-(s + aq): a mixed phase including solid (Na, Mg, Ca)(NO₃, SO₄)·xH₂O and homogeneously
524 crystallized NaCl + aqueous/amorphous (Mg·xH₂O)²⁺ and NO₃⁻/SO₄²⁻, and other minor species
525 below final ERHs = 30.5–17.9% for Cl-depleted SSAs ($X_{(\text{Na, Mg})\text{Cl}} < 0.40$).

526 (v) T-(s): All components are mixed in solid phase at RH = ~14.6–5.0% for all mole fractions of
527 chloride. Amorphous or gel forming Mg(NO₃, SO₄)·xH₂O shows gradual water loss, while only
528 a small amount of MgCl₂·xH₂O is expected to crystallize.

529

530 3.3 Non-SSA particles

531 Generally, mineral particles such as aluminosilicates and calcium carbonate tend to be difficult
532 to absorb water and grow in size with increasing RH. However, these particles can become hygroscopic
533 after reaction with NO_x and SO₂ in the presence of water and/or mixing with SSAs. Particle #14 shown
534 in Fig. 8 is a highly aged aluminosilicate that has mixed with an SSA moiety, probably with (Na, Mg)(Cl,
535 NO₃) and organic species as confirmed using X-ray spectrum. Clear deliquescence and efflorescence
536 transitions are observed in the gradual growth and shrinkage of particle #14 due mainly to the SSA part,
537 and the growth of the aged aluminosilicate is certainly smaller than the SSA at maximum RH. Particle
538 #20 shown in Fig. S6 is a reacted Ca-containing particle with nitrate showing gradual change in size
539 during humidification and dehydration processes, following hygroscopic property reported before (Ahn
540 et al., 2010). Particle #36 is a typical ammonium sulfate mixed with organic species as shown in Fig.
541 S7, and the major chemical components of particle #36 are C, N, O, and S. The particle showed a first
542 partial deliquescence transition at RH = 67.5%, which may be the MDRH for the mixture of ammonium
543 sulfate and organic species. Upon further increase in RH, the particle absorbed more moisture and fully
544 dissolved at RH = 77.1%, which is slightly lower than the DRH of pure ammonium sulfate particles
545 (Wu et al., 2019). During the dehydration process, particle #36 showed a slower rate of shrinkage than
546 ammonium sulfate particles, indicating inhibition of water evaporation due to surface hydrophobic
547 organic moieties, and effloresced at RH = 27.6%, which is lower than the ERH of ammonium sulfate
548 particles (Wu et al., 2019). Some particles, such as reacted Ca-containing particles #17 and #25 and an
549 aged SiO₂ particle #37, exhibit partial dissolution as shown in Fig. S8 and S9. The 2-D area ratio of
550 particle #17 at maximum RH is larger than that of particle #25, indicating the existence of more
551 hygroscopic components in particle #17. Particle #37 showed gradual increase and decrease with partial
552 dissolution only on the right side of particle, possibly due to the reacted Ca-containing one with nitrate
553 moiety. The observation of the hygroscopic behavior of particles having partial growth suggests that a

554 small content of hygroscopic chemical species can control the hygroscopic behavior of particles with
555 major non-hygroscopic species. On the other hand, genuine aluminosilicate particles #29 and #32 (Fig.
556 S10) and Fe-rich particles #2 and #7 (Fig. S11) did not show hygroscopic growth with changing RH.

557

558 **4 Atmospheric Implications**

559 The investigation of the hygroscopic behavior of ambient SSAs is crucial for understanding the
560 atmospheric chemistry and physics of marine environments. Previous studies have recognized that
561 SSAs contain a wide range of inorganic sea salt and organic species (Schiffer et al., 2018), making it
562 difficult to assess their hygroscopicity. In this study, the hygroscopic behavior of SSAs was
563 systematically characterized and correlated with the role of inorganic salt moieties and enriched organic
564 material coating. It was found that SSAs partially dissolve at lower RHs than the inorganic surrogates,
565 including (Na, Mg)(Cl, NO₃), due to the coexistence with other soluble moieties such as water-soluble
566 secondary organics. This indicates that SSAs will be increasingly susceptible to trace gas species and
567 subsequent heterogeneous chemical reactions (Lee et al., 2020). The degree of chloride depletion was
568 also found to affect the hygroscopic behavior of aged SSAs. SSAs with a higher degree of chloride
569 depletion, i.e., higher aging degree, tend to exhibit multiple phase transitions with reducing RH,
570 retaining phase-separated core-shell mixing state, which impacts aerosol-radiation interactions (Sun et
571 al., 2018). The importance of considering these surrogate systems when modeling the hygroscopic
572 behavior of ambient SSAs is apparent, especially in the case of field observations where a wide range
573 of mixing states exist in particles. Even though there are still discrepancies regarding whether the
574 organic fraction can influence the hygroscopic growth of SSAs, this study demonstrated that organic
575 substances covering the sea salt moieties did suppress their hygroscopic growth. Further investigations,
576 including obtaining exact elemental and molecular compositions of the organic shells, are needed to
577 examine the aging of SSAs and quantify their uncertain effects on SSAs' hygroscopicity in
578 thermodynamic models.

579 In addition, other species involving mineral dust and anthropogenic particles can be transported
580 into marine environments and mixed with SSAs, which alter the particle compositions and in turn, their
581 hygroscopicity. Heterogeneous mixing or coating of SSAs onto less hygroscopic dust particles can
582 enhance their ability to interact with water vapor and reactive trace gases, leading to the formation of
583 new particles and increased CCN activity (Tang et al., 2016). This mixing can also affect the optical
584 properties and radiative forcing of atmospheric aerosols, as the scattering and absorption of solar

585 radiation by aerosols are dependent on their size, composition, and mixing state. Furthermore, the
586 impact of anthropogenic emissions on the hygroscopicity of marine aerosols is an important area of
587 research, as increased levels of atmospheric pollutants may enhance the aerosol-water interaction and
588 lead to changes in cloud properties and precipitation patterns (Su et al., 2022). Therefore, a
589 comprehensive understanding of the hygroscopic behavior of marine aerosols and their interactions
590 with other atmospheric constituents is necessary for accurately predicting their impacts on climate and
591 air quality.

592

593 **5 Conclusions**

594 The hygroscopic behavior of individual ambient aerosol particles collected at a coastal site of
595 Jeju Island, Korea, was investigated in correlation with their chemical compositions derived from X-
596 ray microanalysis. Specifically, we focused on the hygroscopic behavior of ambient aged SSAs and
597 their dependence on the extent of reaction between Cl^- and NO_3^- ions, estimated from the mixing ratios
598 of these ions using SEM-EDX. The phase transitions of the aged SSAs were found to be dominated by
599 inorganics involving $\text{Na}(\text{Cl}, \text{NO}_3)$ and/or $(\text{Na}, \text{Mg})(\text{Cl}, \text{NO}_3)$ systems, with organic surfactant films
600 covering the droplets suppressing hygroscopic growth and shrinkage with changing RH. For Cl-rich
601 SSAs, two major transitions were observed during the humidification process, firstly at the MDRH and
602 secondly at a final DRH. During the dehydration process, Cl-rich SSAs showed single-stage
603 efflorescence. Cl-depleted SSAs showed two prompt deliquescence transitions during the
604 humidification process and stepwise transitions during the dehydration process, depending on their
605 chemical compositions.

606 The hygroscopic behavior of other particle types, including aged aluminosilicate, Ca-containing,
607 organic and ammonium sulfate mixture, and Fe-rich particles, was also observed. Aged mineral
608 particles showed varying degrees of size changes with changing RH, potentially due to the presence of
609 SSAs and/or NO_3^- species resulting from coagulation and heterogeneous reactions, while non-reacted
610 mineral and Fe-rich particles did not exhibit significant size changes during the hygroscopic process.
611 The mixture particles of organic and ammonium sulfate displayed lower DRH and ERH values
612 compared to pure ammonium sulfate salt, indicating the impact of organic species on the hygroscopic
613 behavior of ammonium sulfate. While there have been some studies on the hygroscopic behavior of
614 ambient marine aerosols, this study is one of the first to systematically investigate their hygroscopic

615 behavior and to correlate it with their chemical compositions, providing better insights into their impact
616 on climate change and atmospheric chemistry.

617

618 **Data availability**

619 The data used in this study are available upon request; please contact Chul-Un Ro (curo@inha.ac.kr).

620

621 **Author contributions**

622 LW, HJE, HY, DG, and HRC designed the experiment. LW, HJE, HY, and HRC carried out the
623 measurements and/or analyzed the data. LW, HJE, HY, DG, HRC, PF, and CUR contributed discussion
624 of the data. LW, HJE, DG, and CUR drafted the paper.

625

626 **Competing interests**

627 The authors declare that they have no conflict of interest.

628

629 **Acknowledgements**

630 This study was supported by the National Research Foundation of Korea (NRF) grant funded by the
631 Korean government (MSIT) (No. 2021R1A4A1032579 and No. 2021R1A2C2004240) and by the
632 National Institute of Environmental Research (NIER) funded by the Ministry of Environment (MOE)
633 of Korea (NIER-2021-03-03-007).

634

635 **References**

- 636 Ahn, K.-H., Kim, S.-M., Jung, H.-J., Lee, M.-J., Eom, H.-J., Maskey, S., and Ro, C.-U.: Combined Use
637 of Optical and Electron Microscopic Techniques for the Measurement of Hygroscopic Property,
638 Chemical Composition, and Morphology of Individual Aerosol Particles, *Anal. Chem.*, 82, 7999-
639 8009, 10.1021/ac101432y, 2010.
- 640 Ansari, A. S. and Pandis, S. N.: Prediction of multicomponent inorganic atmospheric aerosol behavior,
641 *Atmos. Environ.*, 33, 745-757, [http://dx.doi.org/10.1016/S1352-2310\(98\)00221-0](http://dx.doi.org/10.1016/S1352-2310(98)00221-0), 1999.
- 642 Atkinson, D. B., Radney, J. G., Lum, J., Kolesar, K. R., Cziczo, D. J., Pekour, M. S., Zhang, Q., Setyan,
643 A., Zelenyuk, A., and Cappa, C. D.: Aerosol optical hygroscopicity measurements during the 2010
644 CARES campaign, *Atmos. Chem. Phys.*, 15, 4045-4061, 10.5194/acp-15-4045-2015, 2015.
- 645 Ault, A. P., Guasco, T. L., Baltrusaitis, J., Ryder, O. S., Trueblood, J. V., Collins, D. B., Ruppel, M. J.,
646 Cuadra-Rodriguez, L. A., Prather, K. A., and Grassian, V. H.: Heterogeneous Reactivity of Nitric
647 Acid with Nascent Sea Spray Aerosol: Large Differences Observed between and within Individual
648 Particles, *J. Phys. Chem. Lett.*, 5, 2493-2500, 10.1021/jz5008802, 2014.
- 649 Ault, A. P., Moffet, R. C., Baltrusaitis, J., Collins, D. B., Ruppel, M. J., Cuadra-Rodriguez, L. A., Zhao,
650 D., Guasco, T. L., Ebben, C. J., Geiger, F. M., Bertram, T. H., Prather, K. A., and Grassian, V. H.:

651 Size-Dependent Changes in Sea Spray Aerosol Composition and Properties with Different
652 Seawater Conditions, *Environ. Sci. Technol.*, 47, 5603-5612, 10.1021/es400416g, 2013.

653 Beardsley, R., Jang, M., Ori, B., Im, Y., Delcomyn, C. A., and Witherspoon, N.: Role of sea salt aerosols
654 in the formation of aromatic secondary organic aerosol: yields and hygroscopic properties,
655 *Environ. Chem.*, 10, 167-177, <http://dx.doi.org/10.1071/EN13016>, 2013.

656 Bertram, T. H., Cochran, R. E., Grassian, V. H., and Stone, E. A.: Sea spray aerosol chemical
657 composition: elemental and molecular mimics for laboratory studies of heterogeneous and
658 multiphase reactions, *Chem. Soc. Rev.*, 47, 2374-2400, 10.1039/c7cs00008a, 2018.

659 Carslaw, K. S., Clegg, S. L., and Brimblecombe, P.: A Thermodynamic Model of the System HCl-
660 HNO₃-H₂SO₄-H₂O, Including Solubilities of HBr, from < 200 to 328 K, *J. Phys. Chem. A*, 99,
661 11557-11574, 10.1021/j100029a039, 1995.

662 Chan, C. K., Ha, Z., and Choi, M. Y.: Study of water activities of aerosols of mixtures of sodium and
663 magnesium salts, *Atmos. Environ.*, 34, 4795-4803, 10.1016/S1352-2310(00)00252-1, 2000.

664 Chan, C. K., Liang, Z., Zheng, J., Clegg, S. L., and Brimblecombe, P.: Thermodynamic properties of
665 aqueous aerosols to high supersaturation: I—measurements of water activity of the system
666 Na⁺-Cl⁻-NO₃⁻-SO₄²⁻-H₂O at ~ 298.15 K, *Aerosol Sci. Technol.*, 27, 324-344,
667 10.1080/02786829708965477, 1997.

668 Chang, S.-Y. and Lee, C.-T.: Applying GC-TCD to investigate the hygroscopic characteristics of mixed
669 aerosols, *Atmos. Environ.*, 36, 1521-1530, 10.1016/S1352-2310(01)00546-5, 2002.

670 Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System
671 H⁺-NH₄⁺-Na⁺-SO₄²⁻-NO₃⁻-Cl⁻-H₂O at 298.15 K, *J. Phys. Chem. A*, 102, 2155-2171,
672 10.1021/jp973043j, 1998a.

673 Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System
674 H⁺-NH₄⁺-SO₄²⁻-NO₃⁻-H₂O at Tropospheric Temperatures, *J. Phys. Chem. A*, 102, 2137-2154,
675 10.1021/jp973042r, 1998b.

676 Cochran, R. E., Laskina, O., Jayarathne, T., Laskin, A., Laskin, J., Lin, P., Sultana, C., Lee, C., Moore,
677 K. A., Cappa, C. D., Bertram, T. H., Prather, K. A., Grassian, V. H., and Stone, E. A.: Analysis of
678 Organic Anionic Surfactants in Fine and Coarse Fractions of Freshly Emitted Sea Spray Aerosol,
679 *Environ. Sci. Technol.*, 50, 2477-2486, 10.1021/acs.est.5b04053, 2016.

680 Cochran, R. E., Laskina, O., Trueblood, J. V., Estillore, A. D., Morris, H. S., Jayarathne, T., Sultana, C.
681 M., Lee, C., Lin, P., Laskin, J., Laskin, A., Dowling, J. A., Qin, Z., Cappa, C. D., Bertram, T. H.,
682 Tivanski, A. V., Stone, E. A., Prather, K. A., and Grassian, V. H.: Molecular Diversity of Sea Spray
683 Aerosol Particles: Impact of Ocean Biology on Particle Composition and Hygroscopicity, *Chem*,
684 2, 655-667, 10.1016/j.chempr.2017.03.007, 2017.

685 Cohen, M. D., Flagan, R. C., and Seinfeld, J. H.: Studies of concentrated electrolyte solutions using the
686 electrodynamic balance. 3. Solute nucleation, *J. Phys. Chem*, 91, 4583-4590,
687 10.1021/j100301a031, 1987.

688 Cziczo, D. J., Nowak, J. B., Hu, J. H., and Abbatt, J. P. D.: Infrared spectroscopy of model tropospheric
689 aerosols as a function of relative humidity: Observation of deliquescence and crystallization, *J.*
690 *Geophys. Res. Atmos.*, 102, 18843-18850, 10.1029/97jd01361, 1997.

691 Eom, H.-J., Gupta, D., Li, X., Jung, H.-J., Kim, H., and Ro, C.-U.: Influence of Collecting Substrates
692 on the Characterization of Hygroscopic Properties of Inorganic Aerosol Particles, *Anal. Chem.*,
693 86, 2648-2656, 10.1021/ac4042075, 2014.

694 Eom, H. J., Gupta, D., Cho, H. R., Hwang, H., Hur, S., Gim, Y., and Ro, C. U.: Single-particle
695 investigation of summertime and wintertime Antarctic sea spray aerosols using low-Z particle

696 EPMA, Raman microspectrometry, and ATR-FTIR imaging techniques, *Atmos. Chem. Phys.*,
697 2016, 1-30, 10.5194/acp-2016-584, 2016.

698 Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the upper and lower atmosphere : theory,
699 experiments, and applications, Academic Press, San Diego, 2000.

700 Forestieri, S. D., Cornwell, G. C., Helgestad, T. M., Moore, K. A., Lee, C., Novak, G. A., Sultana, C.
701 M., Wang, X., Bertram, T. H., Prather, K. A., and Cappa, C. D.: Linking variations in sea spray
702 aerosol particle hygroscopicity to composition during two microcosm experiments, *Atmos. Chem.*
703 *Phys.*, 16, 9003-9018, 10.5194/acp-16-9003-2016, 2016.

704 Freney, E. J., Adachi, K., and Buseck, P. R.: Internally mixed atmospheric aerosol particles:
705 Hygroscopic growth and light scattering, *J. Geophys. Res. Atmos.*, 115, D19210,
706 10.1029/2009jd013558, 2010.

707 Gard, E. E., Kleeman, M. J., Gross, D. S., Hughes, L. S., Allen, J. O., Morrical, B. D., Ferguson, D.
708 P., Dienes, T., E. Gälli, M., and Johnson, R. J.: Direct observation of heterogeneous chemistry in
709 the atmosphere, *Science*, 279, 1184-1187, 10.1126/science.279.5354.1184, 1998.

710 Ge, Z., Wexler, A. S., and Johnston, M. V.: Multicomponent Aerosol Crystallization, *J. Colloid Interface*
711 *Sci.*, 183, 68-77, <http://dx.doi.org/10.1006/jcis.1996.0519>, 1996.

712 Ge, Z., Wexler, A. S., and Johnston, M. V.: Deliquescence Behavior of Multicomponent Aerosols, *J.*
713 *Phys. Chem. A*, 102, 173-180, 10.1021/jp972396f, 1998.

714 Geng, H., Hwang, H., Liu, X., Dong, S., and Ro, C. U.: Investigation of aged aerosols in size-resolved
715 Asian dust storm particles transported from Beijing, China, to Incheon, Korea, using low-Z
716 particle EPMA, *Atmos. Chem. Phys.*, 14, 3307-3323, 10.5194/acp-14-3307-2014, 2014.

717 Geng, H., Kang, S., Jung, H. J., Choël, M., Kim, H., and Ro, C. U.: Characterization of individual
718 submicrometer aerosol particles collected in Incheon, Korea, by quantitative transmission electron
719 microscopy energy-dispersive X-ray spectrometry, *J. Geophys. Res. Atmos.*, 115,
720 10.1029/2009JD013486, 2010.

721 Ghorai, S., Wang, B., Tivanski, A., and Laskin, A.: Hygroscopic properties of internally mixed particles
722 composed of NaCl and water-soluble organic acids, *Environ. Sci. Technol.*, 48, 2234-2241,
723 10.1021/es404727u, 2014.

724 Guo, L., Gu, W., Peng, C., Wang, W., Li, Y. J., Zong, T., Tang, Y., Wu, Z., Lin, Q., Ge, M., Zhang, G.,
725 Hu, M., Bi, X., Wang, X., and Tang, M.: A comprehensive study of hygroscopic properties of
726 calcium- and magnesium-containing salts: implication for hygroscopicity of mineral dust and sea
727 salt aerosols, *Atmos. Chem. Phys.*, 19, 2115-2133, 10.5194/acp-19-2115-2019, 2019.

728 Gupta, D., Eom, H. J., Cho, H. R., and Ro, C. U.: Hygroscopic behavior of NaCl-MgCl₂ mixture
729 particles as nascent sea-spray aerosol surrogates and observation of efflorescence during
730 humidification, *Atmos. Chem. Phys.*, 15, 11273-11290, 10.5194/acp-15-11273-2015, 2015a.

731 Gupta, D., Kim, H., Park, G., Li, X., Eom, H. J., and Ro, C. U.: Hygroscopic properties of NaCl and
732 NaNO₃ mixture particles as reacted inorganic sea-salt aerosol surrogates, *Atmos. Chem. Phys.*, 15,
733 3379-3393, 10.5194/acp-15-3379-2015, 2015b.

734 Haynes, W. M.: CRC Handbook of Chemistry and Physics, 96th Edition, CRC Press, Boca Raton,
735 Florida, 14-18, 2015.

736 Haywood, J. and Boucher, O.: Estimates of the direct and indirect radiative forcing due to tropospheric
737 aerosols: A review, *Rev. Geophys.*, 38, 513-543, 10.1029/1999rg000078, 2000.

738 Herich, H., Kammermann, L., Friedman, B., Gross, D. S., Weingartner, E., Lohmann, U., Spichtinger,
739 P., Gysel, M., Baltensperger, U., and Cziczo, D. J.: Subarctic atmospheric aerosol composition: 2.
740 Hygroscopic growth properties, *J. Geophys. Res. Atmos.*, 114, D13204, 10.1029/2008jd011574,
741 2009.

742 Keene, W. C., Maring, H., Maben, J. R., Kieber, D. J., Pszenny, A. A. P., Dahl, E. E., Izaguirre, M. A.,
743 Davis, A. J., Long, M. S., Zhou, X., Smoydzin, L., and Sander, R.: Chemical and physical
744 characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface, *J.*
745 *Geophys. Res. Atmos.*, 112, D21202, 10.1029/2007jd008464, 2007.

746 Kim, H., Lee, M.-J., Jung, H.-J., Eom, H.-J., Maskey, S., Ahn, K.-H., and Ro, C.-U.: Hygroscopic
747 behavior of wet dispersed and dry deposited NaNO₃ particles, *Atmos. Environ.*, 60, 68-75,
748 <http://dx.doi.org/10.1016/j.atmosenv.2012.06.011>, 2012.

749 Kong, X., Wolf, M. J., Roesch, M., Thomson, E. S., Bartels-Rausch, T., Alpert, P. A., Ammann, M.,
750 Prisle, N. L., and Cziczo, D. J.: A continuous flow diffusion chamber study of sea salt particles
751 acting as cloud nuclei: deliquescence and ice nucleation, *Tellus B: Chem. Phys. Meteorol.*, 70, 1-
752 11, 10.1080/16000889.2018.1463806, 2018.

753 Krieger, U. K., Marcolli, C., and Reid, J. P.: Exploring the complexity of aerosol particle properties and
754 processes using single particle techniques, *Chem. Soc. Rev.*, 41, 6631-6662, 10.1039/c2cs35082c,
755 2012.

756 Krueger, B. J., Grassian, V. H., Iedema, M. J., Cowin, J. P., and Laskin, A.: Probing Heterogeneous
757 Chemistry of Individual Atmospheric Particles Using Scanning Electron Microscopy and Energy-
758 Dispersive X-ray Analysis, *Anal. Chem.*, 75, 5170-5179, 10.1021/ac034455t, 2003.

759 Laskin, A., Moffet, R. C., Gilles, M. K., Fast, J. D., Zaveri, R. A., Wang, B., Nigge, P., and
760 Shutthanandan, J.: Tropospheric chemistry of internally mixed sea salt and organic particles:
761 Surprising reactivity of NaCl with weak organic acids, *J. Geophys. Res. Atmos.*, 117, Tropospheric
762 chemistry of internally mixed sea salt and organic particles: Surprising reactivity of NaCl with
763 weak organic acids, 2012.

764 Lee, H. D., Morris, H. S., Laskina, O., Sultana, C. M., Lee, C., Jayarathne, T., Cox, J. L., Wang, X.,
765 Hasenecz, E. S., DeMott, P. J., Bertram, T. H., Cappa, C. D., Stone, E. A., Prather, K. A., Grassian,
766 V. H., and Tivanski, A. V.: Organic Enrichment, Physical Phase State, and Surface Tension
767 Depression of Nascent Core-Shell Sea Spray Aerosols during Two Phytoplankton Blooms, *ACS*
768 *Earth Space Chem.*, 4, 650-660, 10.1021/acsearthspacechem.0c00032, 2020.

769 Li, X., Wu, L., Lee, J.-S., and Ro, C.-U.: Hygroscopic behavior and chemical reactivity of aerosols
770 generated from mixture solutions of low molecular weight dicarboxylic acids and NaCl, *Phys.*
771 *Chem. Chem. Phys.*, 23, 11052-11064, 10.1039/d1cp00590a, 2021.

772 Li, X., Gupta, D., Eom, H.-J., Kim, H., and Ro, C.-U.: Deliquescence and efflorescence behavior of
773 individual NaCl and KCl mixture aerosol particles, *Atmos. Environ.*, 82, 36-43,
774 <http://dx.doi.org/10.1016/j.atmosenv.2013.10.011>, 2014.

775 Li, Y. J., Liu, P. F., Bergoend, C., Bateman, A. P., and Martin, S. T.: Rebounding hygroscopic inorganic
776 aerosol particles: Liquids, gels, and hydrates, *Aerosol Sci. Technol.*, 51, 388-396,
777 10.1080/02786826.2016.1263384, 2016.

778 Liu, Y. and Laskin, A.: Hygroscopic Properties of CH₃SO₃Na, CH₃SO₃NH₄, (CH₃SO₃)₂Mg, and
779 (CH₃SO₃)₂Ca Particles Studied by micro-FTIR Spectroscopy, *J. Phys. Chem. A*, 113, 1531-1538,
780 10.1021/jp8079149, 2009.

781 Liu, Y., Cain, J. P., Wang, H., and Laskin, A.: Kinetic Study of Heterogeneous Reaction of Deliquesced
782 NaCl Particles with Gaseous HNO₃ Using Particle-on-Substrate Stagnation Flow Reactor
783 Approach, *J. Phys. Chem. A*, 111, 10026-10043, 10.1021/jp072005p, 2007.

784 Liu, Y., Minofar, B., Desyaterik, Y., Dames, E., Zhu, Z., Cain, J. P., Hopkins, R. J., Gilles, M. K., Wang,
785 H., and Jungwirth, P.: Internal structure, hygroscopic and reactive properties of mixed sodium
786 methanesulfonate-sodium chloride particles, *Phys. Chem. Chem. Phys.*, 13, 11846-11857,
787 10.1039/C1CP20444K, 2011.

788 Martin, S. T.: Phase Transitions of Aqueous Atmospheric Particles, *Chem. Rev.*, 100, 3403-3454,
789 10.1021/cr990034t, 2000.

790 Meskhidze, N., Petters, M. D., Tsigaridis, K., Bates, T., O'Dowd, C., Reid, J., Lewis, E. R., Gantt, B.,
791 Anguelova, M. D., Bhave, P. V., Bird, J., Callaghan, A. H., Ceburnis, D., Chang, R., Clarke, A.,
792 de Leeuw, G., Deane, G., DeMott, P. J., Elliot, S., Facchini, M. C., Fairall, C. W., Hawkins, L.,
793 Hu, Y., Hudson, J. G., Johnson, M. S., Kaku, K. C., Keene, W. C., Kieber, D. J., Long, M. S.,
794 Mårtensson, M., Modini, R. L., Osburn, C. L., Prather, K. A., Pszenny, A., Rinaldi, M., Russell, L.
795 M., Salter, M., Sayer, A. M., Smirnov, A., Suda, S. R., Toth, T. D., Worsnop, D. R., Wozniak, A.,
796 and Zorn, S. R.: Production mechanisms, number concentration, size distribution, chemical
797 composition, and optical properties of sea spray aerosols, *Atmos. Sci. Lett.*, 14, 207-213,
798 10.1002/asl2.441, 2013.

799 Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol
800 particles interacting with water vapor: conceptual framework and experimental evidence for
801 restructuring, phase transitions and kinetic limitations, *Atmos. Chem. Phys*, 9, 9491-9522,
802 10.5194/acp-9-9491-2009, 2009.

803 Ming, Y. and Russell, L. M.: Predicted hygroscopic growth of sea salt aerosol, *J. Geophys. Res. Atmos.*,
804 106, 28259-28274, 10.1029/2001jd000454, 2001.

805 Nguyen, Q. T., Kjær, K. H., Kling, K. I., Boesen, T., and Bilde, M.: Impact of fatty acid coating on the
806 CCN activity of sea salt particles, *Tellus B: Chem. Phys. Meteorol.*, 69, 1304064,
807 10.1080/16000889.2017.1304064, 2017.

808 Niedermeier, D., Wex, H., Voigtländer, J., Stratmann, F., Brüggemann, E., Kiselev, A., Henk, H., and
809 Heintzenberg, J.: LACIS-measurements and parameterization of sea-salt particle hygroscopic
810 growth and activation, *Atmos. Chem. Phys.*, 8, 579-590, 10.5194/acp-8-579-2008, 2008.

811 O'Dowd, C. D. and de Leeuw, G.: Marine aerosol production: a review of the current knowledge, *Philos.*
812 *trans., Math. phys. eng. sci.*, 365, 1753-1774, 10.1098/rsta.2007.2043, 2007.

813 Pandis, S. N., Wexler, A. S., and Seinfeld, J. H.: Dynamics of Tropospheric Aerosols, *J. Phys. Chem.*,
814 99, 9646-9659, 10.1021/j100024a003, 1995.

815 Pöschl, U. and Shiraiwa, M.: Multiphase Chemistry at the Atmosphere–Biosphere Interface Influencing
816 Climate and Public Health in the Anthropocene, *Chem. Rev.*, 115, 4440-4475, 10.1021/cr500487s,
817 2015.

818 Pósfai, M., Anderson, J. R., Buseck, P. R., and Sievering, H.: Compositional variations of sea-salt-mode
819 aerosol particles from the North Atlantic, *J. Geophys. Res. Atmos.*, 100, 23063-23074,
820 10.1029/95jd01636, 1995.

821 Prather, K. A., Bertram, T. H., Grassian, V. H., Deane, G. B., Stokes, M. D., DeMott, P. J., Aluwihare,
822 L. I., Palenik, B. P., Azam, F., Seinfeld, J. H., Moffet, R. C., Molina, M. J., Cappa, C. D., Geiger,
823 F. M., Roberts, G. C., Russell, L. M., Ault, A. P., Baltrusaitis, J., Collins, D. B., Corrigan, C. E.,
824 Cuadra-Rodriguez, L. A., Ebben, C. J., Forestieri, S. D., Guasco, T. L., Hersey, S. P., Kim, M. J.,
825 Lambert, W. F., Modini, R. L., Mui, W., Pedler, B. E., Ruppel, M. J., Ryder, O. S., Schoepp, N. G.,
826 Sullivan, R. C., and Zhao, D.: Bringing the ocean into the laboratory to probe the chemical
827 complexity of sea spray aerosol, *Proc. Natl. Acad. Sci. USA*, 110, 7550-7555,
828 10.1073/pnas.1300262110, 2013.

829 Quinn, P. K., Collins, D. B., Grassian, V. H., Prather, K. A., and Bates, T. S.: Chemistry and Related
830 Properties of Freshly Emitted Sea Spray Aerosol, *Chem. Rev.*, 10.1021/cr500713g, 2015.

831 Rosati, B., Christiansen, S., Dinesen, A., Roldin, P., Massling, A., Nilsson, E. D., and Bilde, M.: The
832 impact of atmospheric oxidation on hygroscopicity and cloud droplet activation of inorganic sea
833 spray aerosol, *Sci. Rep.*, 11, 10008, 10.1038/s41598-021-89346-6, 2021.

834 Ryder, O. S., Ault, A. P., Cahill, J. F., Guasco, T. L., Riedel, T. P., Cuadra-Rodriguez, L. A., Gaston, C.
835 J., Fitzgerald, E., Lee, C., Prather, K. A., and Bertram, T. H.: On the Role of Particle Inorganic
836 Mixing State in the Reactive Uptake of N_2O_5 to Ambient Aerosol Particles, *Environ. Sci. Technol.*,
837 48, 1618-1627, 10.1021/es4042622, 2014.

838 Saul, T. D., Tolocka, M. P., and Johnston, M. V.: Reactive Uptake of Nitric Acid onto Sodium Chloride
839 Aerosols Across a Wide Range of Relative Humidities, *J. Phys. Chem. A*, 110, 7614-7620,
840 10.1021/jp060639a, 2006.

841 Schiffer, J. M., Mael, L. E., Prather, K. A., Amaro, R. E., and Grassian, V. H.: Sea Spray Aerosol: Where
842 Marine Biology Meets Atmospheric Chemistry, *ACS Cent. Sci.*, 4, 1617-1623,
843 10.1021/acscentsci.8b00674, 2018.

844 Schill, S. R., Collins, D. B., Lee, C., Morris, H. S., Novak, G. A., Prather, K. A., Quinn, P. K., Sultana,
845 C. M., Tivanski, A. V., Zimmermann, K., Cappa, C. D., and Bertram, T. H.: The Impact of Aerosol
846 Particle Mixing State on the Hygroscopicity of Sea Spray Aerosol, *ACS Cent. Sci.*, 1, 132-141,
847 10.1021/acscentsci.5b00174, 2015.

848 Schindelholz, E., Risteen, B., and Kelly, R.: Effect of relative humidity on corrosion of steel under sea
849 salt aerosol proxies: I. NaCl, *J. Electrochem. Soc.*, 161, C450, 10.1149/2.0221410jes, 2014.

850 Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate
851 change, 2nd ed., J. Wiley, Hoboken NJ, 1203 pp., 2006.

852 Semeniuk, T. A., Wise, M. E., Martin, S. T., Russell, L. M., and Buseck, P. R.: Water uptake
853 characteristics of individual atmospheric particles having coatings, *Atmos. Environ.*, 41, 6225-
854 6235, 10.1016/j.atmosenv.2007.04.001, 2007.

855 Song, Y., Li, J., Tsona, N. T., Liu, L., and Du, L.: Enrichment of short-chain organic acids transferred
856 to submicron sea spray aerosols, *Sci. Total Environ.*, 851, 158122,
857 10.1016/j.scitotenv.2022.158122, 2022.

858 Su, B., Wang, T., Zhang, G., Liang, Y., Lv, C., Hu, Y., Li, L., Zhou, Z., Wang, X., and Bi, X.: A review
859 of atmospheric aging of sea spray aerosols: Potential factors affecting chloride depletion, *Atmos.*
860 *Environ.*, 290, 10.1016/j.atmosenv.2022.119365, 2022.

861 Sun, J., Liu, L., Xu, L., Wang, Y., Wu, Z., Hu, M., Shi, Z., Li, Y., Zhang, X., Chen, J., and Li W.: Key
862 role of nitrate in phase transitions of urban particles: implications of important reactive surfaces
863 for secondary aerosol formation, *J. Geophys. Res. Atmos.*, 123, 1234-1243,
864 10.1002/2017JD027264, 2018.

865 Tang, I. N., Tridico, A. C., and Fung, K. H.: Thermodynamic and optical properties of sea salt aerosols,
866 *J. Geophys. Res. Atmos.*, 102, 23269-23275, 10.1029/97jd01806, 1997.

867 Tang, M., Cziczo, D. J., and Grassian, V. H.: Interactions of water with mineral dust aerosol: water
868 adsorption, hygroscopicity, cloud condensation, and ice nucleation, *Chem. Rev.*, 116, 4205-4259,
869 10.1021/acs.chemrev.5b00529, 2016.

870 ten Brink, H. M.: Reactive uptake of HNO_3 and H_2SO_4 in sea-salt (NaCl) particles, *J. Aerosol Sci.*, 29,
871 57-64, [http://dx.doi.org/10.1016/S0021-8502\(97\)00460-6](http://dx.doi.org/10.1016/S0021-8502(97)00460-6), 1998.

872 Tobon, Y. A., El Hajj, D., Seng, S., Bengrad, F., Moreau, M., Visez, N., Chiapello, I., Crumeyrolle, S.,
873 and Choel, M.: Impact of the particle mixing state on the hygroscopicity of internally mixed
874 sodium chloride-ammonium sulfate single droplets: a theoretical and experimental study, *Phys.*
875 *Chem. Chem. Phys.*, 23, 14391-14403, 10.1039/d1cp01574e, 2021.

876 Vaishya, A., Ovadnevaite, J., Bialek, J., Jennings, S. G., Ceburnis, D., and O'Dowd, C. D.: Bistable
877 effect of organic enrichment on sea spray radiative properties, *Geophys. Res. Lett.*, 40, 6395-6398,
878 10.1002/2013gl058452, 2013.

879 Vekemans, B., Janssens, K., Vincze, L., Adams, F., and Van Espen, P.: Analysis of X-ray spectra by
880 iterative least squares (AXIL): New developments, *Xray Spectrom.*, 23, 278-285,
881 10.1002/xrs.1300230609, 1994.

882 Wang, J. and Martin, S. T.: Satellite characterization of urban aerosols: Importance of including
883 hygroscopicity and mixing state in the retrieval algorithms, *J. Geophys. Res. Atmos.*, 112, D17203,
884 10.1029/2006jd008078, 2007.

885 Wang, X., Sultana, C. M., Trueblood, J., Hill, T. C., Malfatti, F., Lee, C., Laskina, O., Moore, K. A.,
886 Beall, C. M., and McCluskey, C. S.: Microbial control of sea spray aerosol composition: A tale of
887 two blooms, *ACS Central Science*, 1, 124-131, 10.1021/acscentsci.5b00148, 2015.

888 Wang, X., Deane, G. B., Moore, K. A., Ryder, O. S., Stokes, M. D., Beall, C. M., Collins, D. B.,
889 Santander, M. V., Burrows, S. M., Sultana, C. M., and Prather, K. A.: The role of jet and film drops
890 in controlling the mixing state of submicron sea spray aerosol particles, *Proc. Natl. Acad. Sci.*
891 *USA*, 114, 6978-6983, 10.1073/pnas.1702420114, 2017.

892 Wexler, A. S. and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H^+ , NH_4^+ ,
893 Na^+ , SO_4^{2-} , NO_3^- , Cl^- , Br^- , and H_2O , *J. Geophys. Res. A*, 107, D14, 4207, 10.1029/2001jd000451,
894 2002.

895 Wexler, A. S. and Seinfeld, J. H.: Second-generation inorganic aerosol model, *Atmos. Environ.*, 27A,
896 25, 2731-2748, 10.1016/0960-1686(91)90203-J, 1991.

897 Wise, M. E., Semeniuk, T. A., Bruintjes, R., Martin, S. T., Russell, L. M., and Buseck, P. R.:
898 Hygroscopic behavior of NaCl-bearing natural aerosol particles using environmental transmission
899 electron microscopy, *J. Geophys. Res. Atmos.*, 112, D10224, 10.1029/2006jd007678, 2007.

900 Wise, M. E., Freney, E. J., Tyree, C. A., Allen, J. O., Martin, S. T., Russell, L. M., and Buseck, P. R.:
901 Hygroscopic behavior and liquid-layer composition of aerosol particles generated from natural
902 and artificial seawater, *J. Geophys. Res. Atmos.*, 114, D03201, 10.1029/2008jd010449, 2009.

903 Woods, E., Chung, D., Lanney, H. M., and Ashwell, B. A.: Surface Morphology and Phase Transitions
904 in Mixed NaCl/MgSO₄ Aerosol Particles, *J. Phys. Chem. A*, 114, 2837-2844, 10.1021/jp911133j,
905 2010.

906 Woods, E., Heylman, K. D., Gibson, A. K., Ashwell, A. P., and Rossi, S. R.: Effects of NO_y Aging on
907 the Dehydration Dynamics of Model Sea Spray Aerosol, *J. Phys. Chem. A*, 117, 4214-4222,
908 10.1021/jp401646d, 2013.

909 Wu, L., Li, X., and Ro, C.-U.: Hygroscopic Behavior of Ammonium Sulfate, Ammonium Nitrate, and
910 their Mixture Particles, *Asian J. Atmos.*, 13, 196-211, 10.5572/ajae.2019.13.3.196, 2019.

911 Wu, L., Becote, C., Sobanska, S., Flaud, P.-M., Perraudin, E., Villenave, E., Song, Y.-C., and Ro, C.-
912 U.: Hygroscopic behavior of aerosols generated from solutions of 3-methyl-1,2,3-
913 butanetricarboxylic acid, its sodium salts, and its mixtures with NaCl, *Atmos. Chem. Phys.*, 20,
914 14103-14122, 10.5194/acp-20-14103-2020, 2020.

915 Xiao, H.-S., Dong, J.-L., Wang, L.-Y., Zhao, L.-J., Wang, F., and Zhang, Y.-H.: Spatially resolved
916 micro-raman observation on the phase separation of effloresced sea salt droplets, *Environ. Sci.*
917 *Technol.*, 42, 8698-8702, 10.1021/es801181f, 2008.

918 Xu, W., Ovadnevaite, J., Fossum, K. N., Lin, C., Huang, R.-J., O'Dowd, C., and Ceburnis, D.: Aerosol
919 hygroscopicity and its link to chemical composition in the coastal atmosphere of Mace Head:
920 marine and continental air masses, *Atmos. Chem. Phys.*, 20, 3777-3791, 10.5194/acp-20-3777-
921 2020, 2020.

922 Zhang, X., Massoli, P., Quinn, P. K., Bates, T. S., and Cappa, C. D.: Hygroscopic growth of submicron
923 and supermicron aerosols in the marine boundary layer, *J. Geophys. Res. Atmos.*, 119, 8384-8399,
924 10.1002/2013jd021213, 2014.

925 Zhang, Y.-H., Choi, M. Y., and Chan, C. K.: Relating Hygroscopic Properties of Magnesium Nitrate to
926 the Formation of Contact Ion Pairs, *J. Phys. Chem. A*, 108, 1712-1718, 10.1021/jp036524d, 2004.
927 Zhao, L.-J., Zhang, Y.-H., Wei, Z.-F., Cheng, H., and Li, X.-H.: Magnesium Sulfate Aerosols Studied
928 by FTIR Spectroscopy: Hygroscopic Properties, Supersaturated Structures, and Implications for
929 Seawater Aerosols, *J. Phys. Chem. A*, 110, 951-958, 10.1021/jp055291i, 2006.
930 Zieger, P., Vaisanen, O., Corbin, J. C., Partridge, D. G., Bastelberger, S., Mousavi-Fard, M., Rosati, B.,
931 Gysel, M., Krieger, U. K., Leck, C., Nenes, A., Riipinen, I., Virtanen, A., and Salter, M. E.:
932 Revising the hygroscopicity of inorganic sea salt particles, *Nat. Commun.*, 8, 15883,
933 10.1038/ncomms15883, 2017.
934 Zuend, A., Marcolli, C., Luo, B. P., and Peter, T.: A thermodynamic model of mixed organic-inorganic
935 aerosols to predict activity coefficients, *Atmos. Chem. Phys.*, 8, 4559–4593, 10.5194/acp-8-4559-
936 2008, 2008.
937 Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O.,
938 McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the
939 thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic
940 mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic
941 functional groups, *Atmos. Chem. Phys.*, 11, 9155–9206, 10.5194/acp-11-9155-2011, 2011.
942

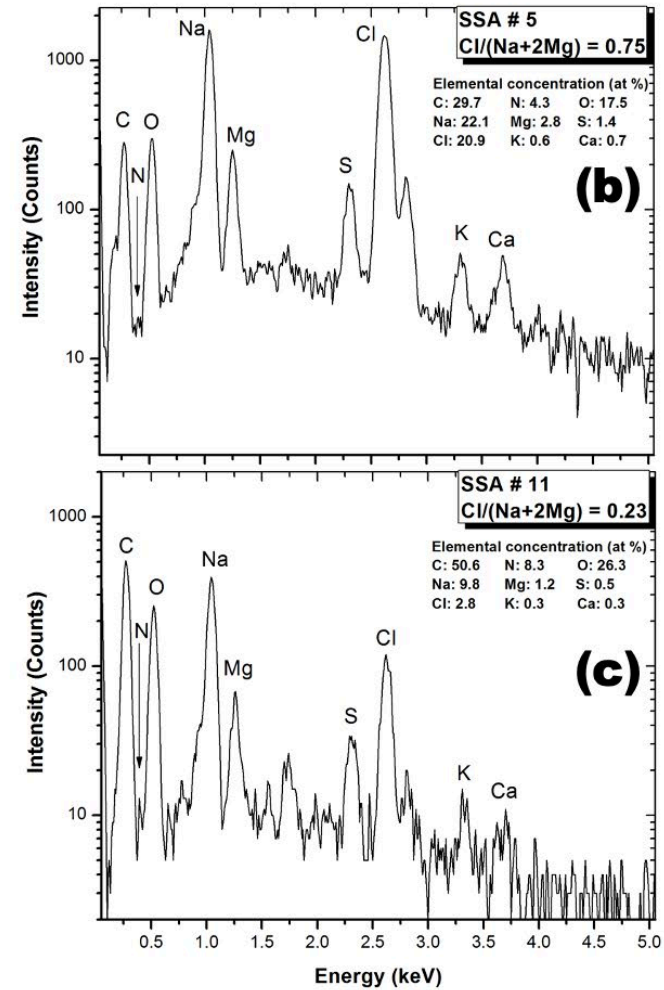
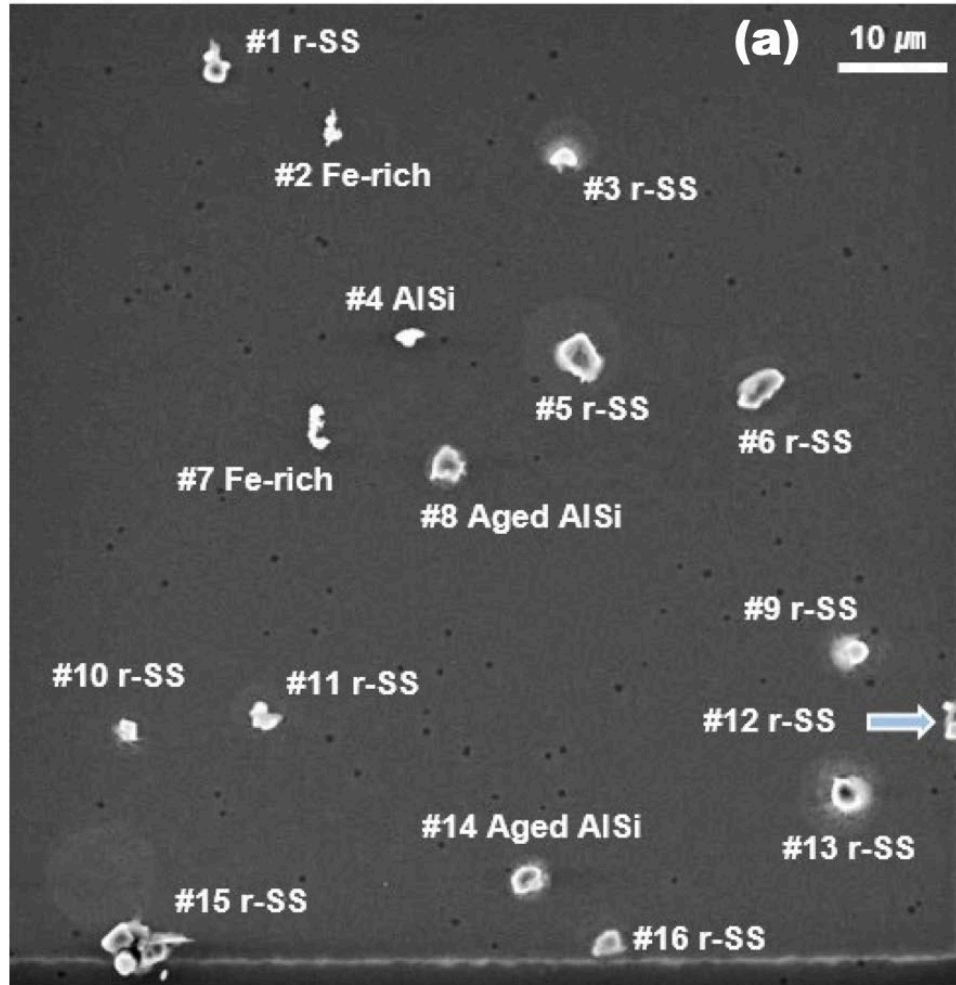
943 **Figure 1.** Location of Gosan sampling site on Jeju Island, South Korea. (Map Copyright © Google Earth)



944

945

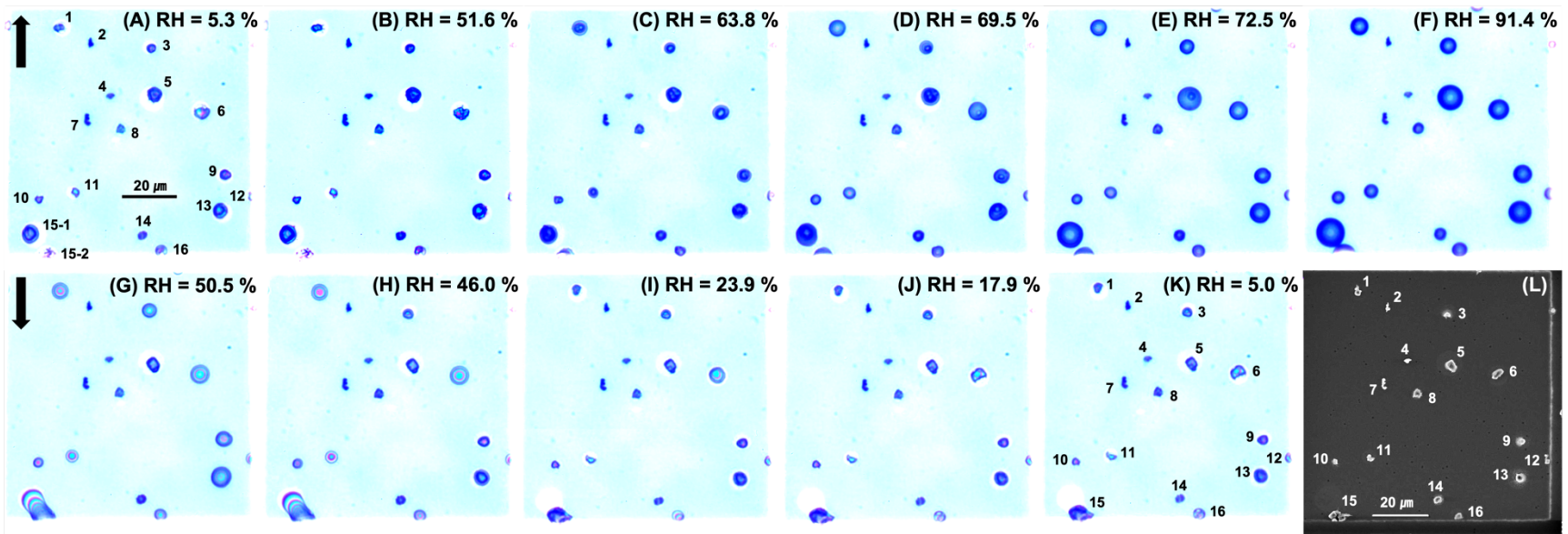
946 **Figure 2.** (a) Secondary electron image (SEI) of the first field containing 16 particles and X-ray spectra of (b) a Cl-
 947 depleted aged SSAs (particles #5 and #11, respectively). In this image, aged SSAs, Fe-containing particles, and aluminosilicates are
 948 denoted as “r-SS”, “Fe-rich”, and “AlSi”, respectively.



949

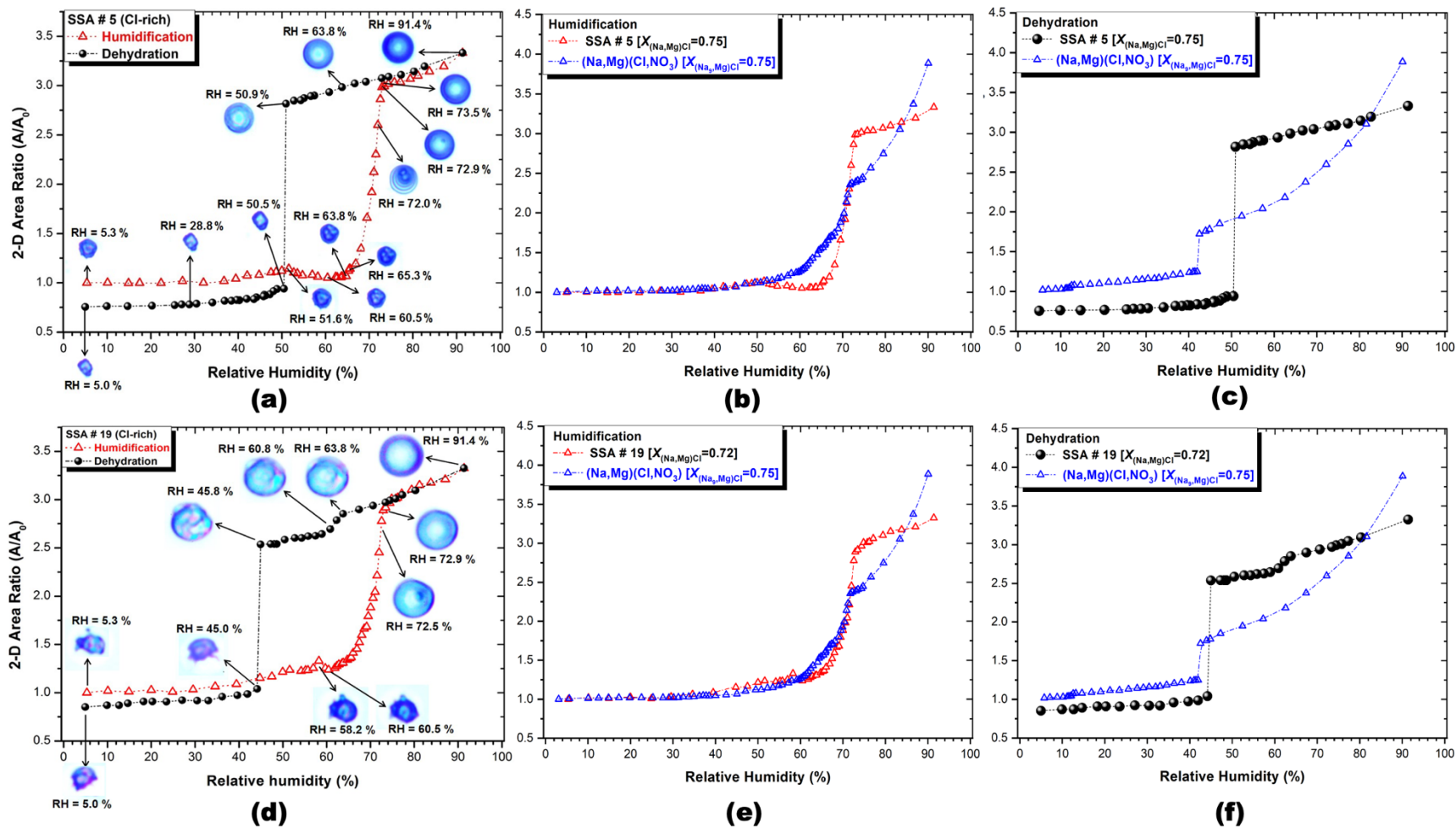
950

951 **Figure 3.** Optical images of the first field on TEM grid during humidifying (A-F, ↑) and dehydration (G-K, ↓) processes and the SEI
952 of the same field (L).



953

954 **Figure 4.** 2-D area ratio plot and optical images of Cl-rich SSAs #5 and #19 (a and d), 2-D area ratio plots of humidification (b and e)
 955 and dehydration (c and f) for the SSAs and $(\text{Na,Mg})(\text{Cl,NO}_3)$ particle as a function of RH.

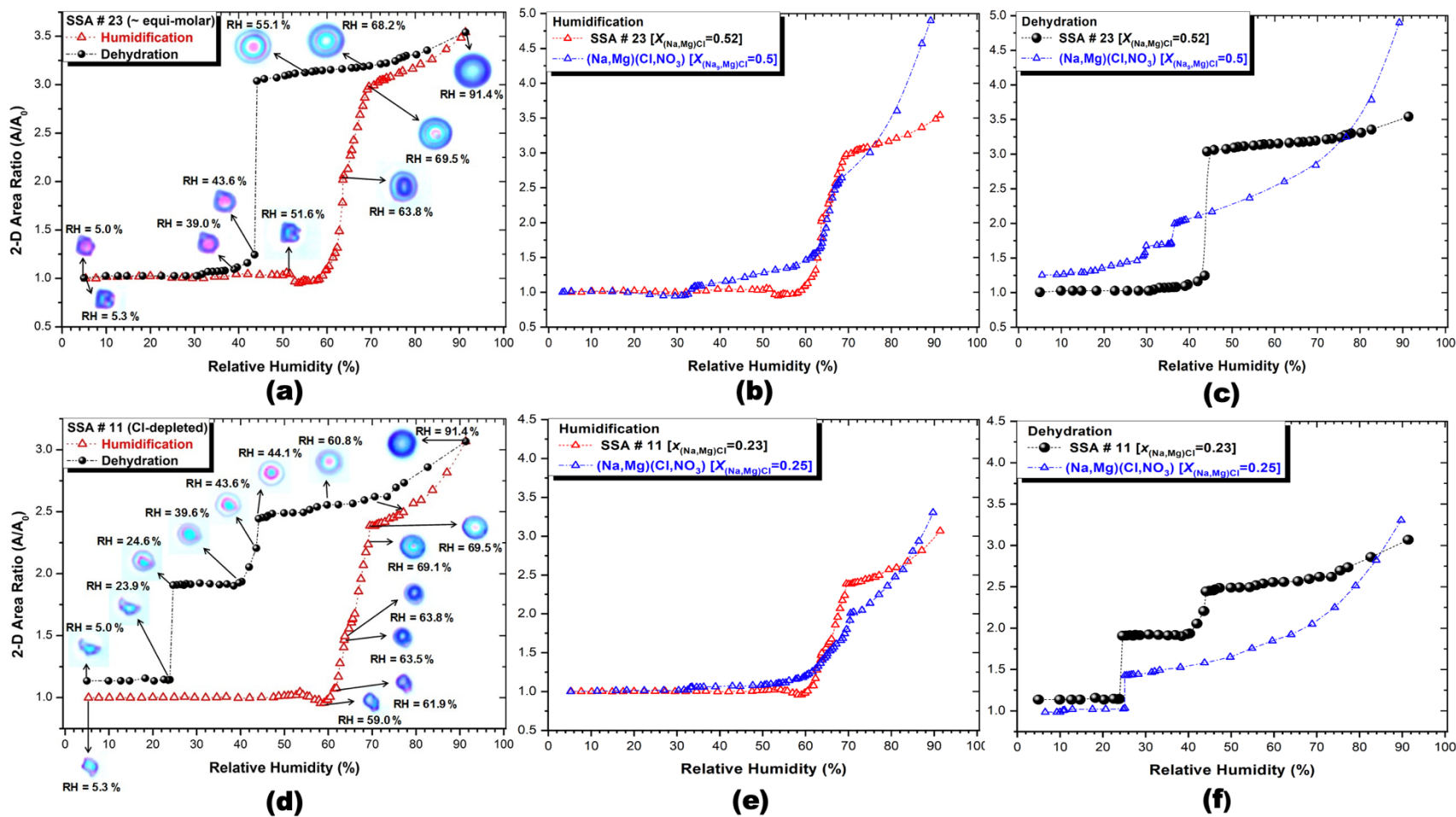


956

957

958

959 **Figure 5.** 2-D area ratio plot and optical images of an equimolar SSA #23 and a Cl-depleted SSA #11 (a and d), 2-D area ratio plots of
 960 humidification (b and e) and dehydration (c and f) for the SSAs and $(\text{Na},\text{Mg})(\text{Cl},\text{NO}_3)$ particles as a function of RH.

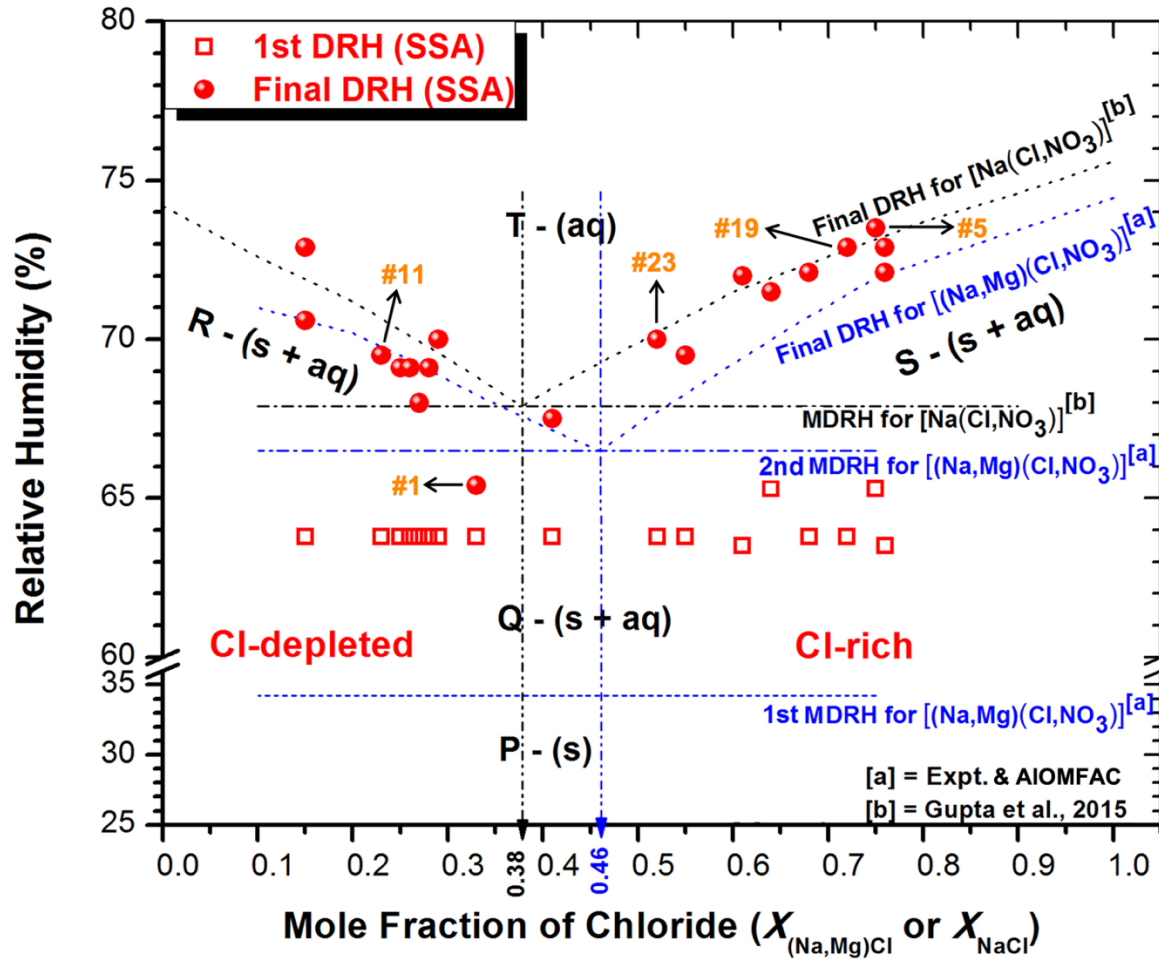


961

962

963

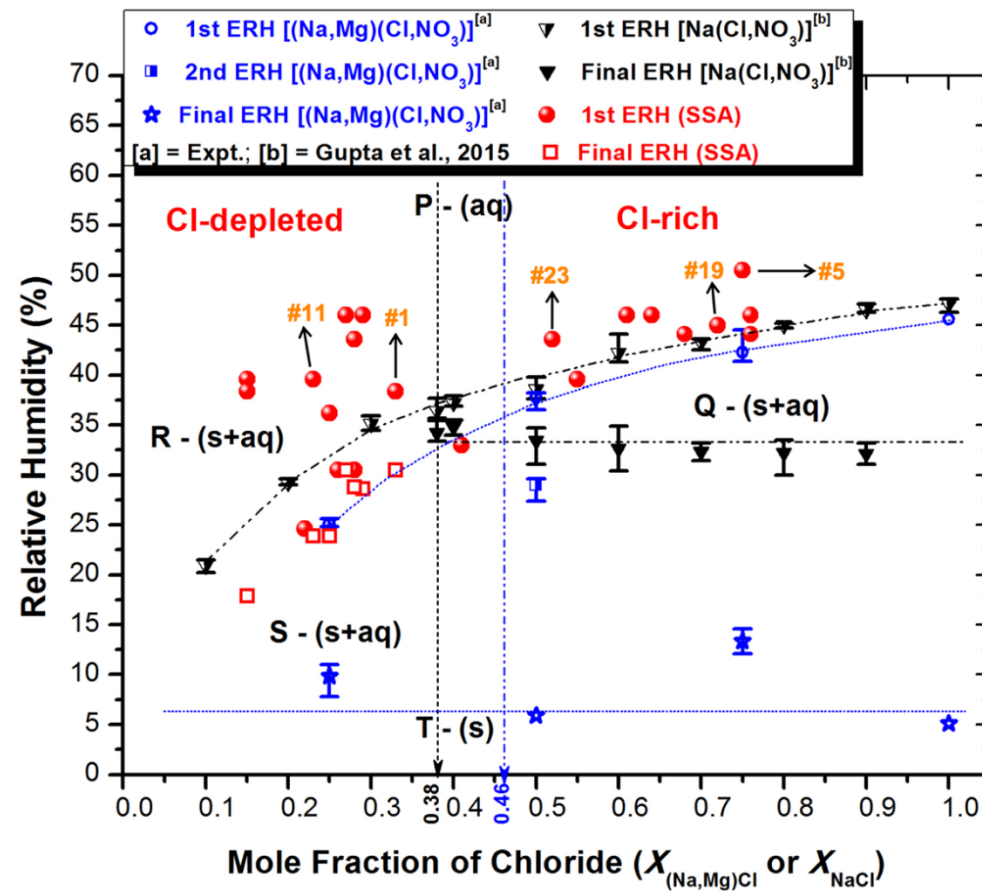
964 **Figure 6.** DRHs of ambient SSAs and (Na, Mg)(Cl, NO₃) and Na(Cl, NO₃) systems calculated from AIOMFAC plotted against the mole
 965 fraction of chloride [$X_{(Na, Mg)Cl}$ or X_{NaCl}]. Major chemical components in each phase: P - all in solid phase; Q - aqueous eutonic
 966 components + NaCl and (Na, Mg, Ca)(NO₃, SO₄, organics) in solid phase; R - NaNO₃ and (Ca, Na)SO₄ in solid phase + aqueous eutonic
 967 components; S - NaCl and (Ca, Na)SO₄ in solid phase + aqueous eutonic components; T - aqueous phase for most components; black
 968 vertical line – a eutonic composition of Na(Cl, NO₃) system; blue vertical line – a eutonic composition of (Na, Mg)(Cl, NO₃) system.



969

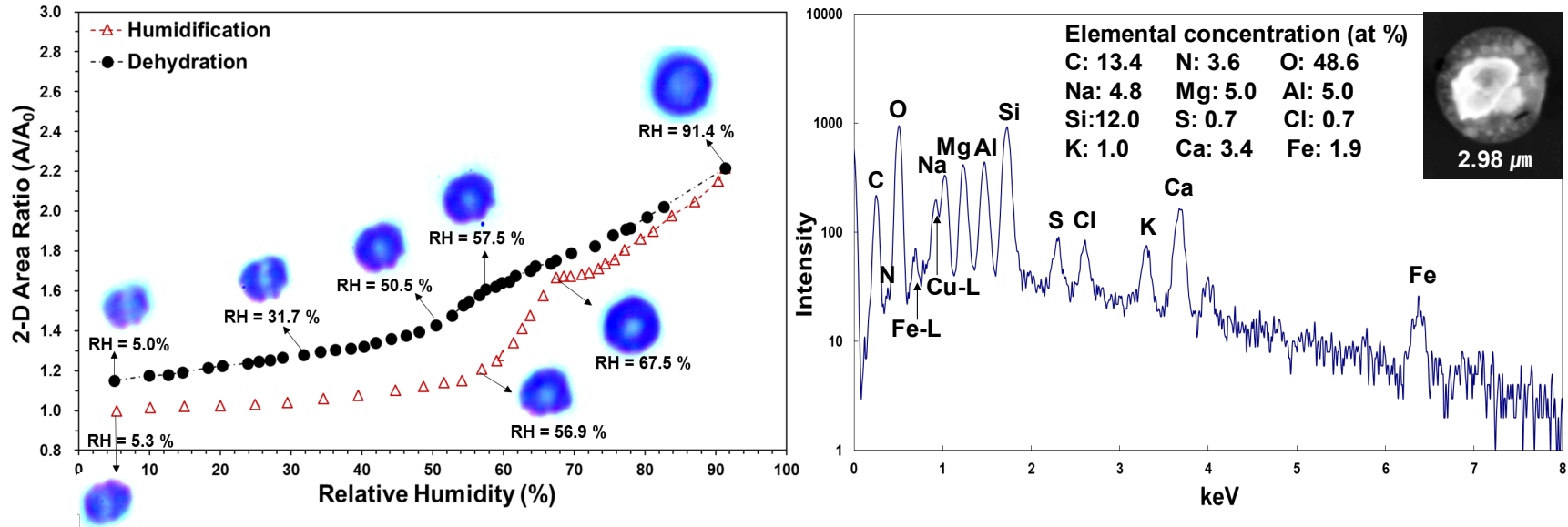
970 **Figure 7.** ERHs of ambient SSAs and those experimentally determined for (Na, Mg)(Cl, NO₃) and Na(Cl, NO₃) systems plotted against
 971 the mole fraction of chloride [$X_{(\text{Na},\text{Mg})\text{Cl}}$ or X_{NaCl}]. Major chemical components in each phase: P – almost all components in aqueous phase;
 972 Q - NaCl and other heterogeneously crystallized moieties in solid phase + aqueous nucleating species like $(\text{Mg}\cdot x\text{H}_2\text{O})^{2+}$ and $\text{Cl}^-/\text{NO}_3^-$
 973 / SO_4^{2-} ; R - heterogeneously crystallized (Na, Mg)NO₃·xH₂O on crystalline (Ca, Na)SO₄(xH₂O) seeds + aqueous NaCl and other
 974 moieties; S - solid (Na, Mg, Ca)(NO₃, SO₄)·xH₂O and homogeneously crystallized NaCl + aqueous/amorphous $(\text{Mg}\cdot x\text{H}_2\text{O})^{2+}$ and NO_3^-
 975 / SO_4^{2-} , and other minor species; T - all in solid phase; black vertical line - a eutonic composition of Na(Cl, NO₃) system; blue vertical
 976 line - a eutonic composition of (Na, Mg)(Cl, NO₃) system.

977



978

979 **Figure 8.** 2-D area ratio plot, X-ray spectrum, and SEM image with diameter of an aged aluminosilicate particle mixed with SSA (part
 980 icle #14)



981

982