Acp-2015-417-revision

Comments (in *italics*), responses, and marked-up revised manuscript

General Comments from Anonymous referee #1

Gupta et al., present observations of the hygroscopic behaviour of NaCl–MgCl₂ mixtures using optical microscopy, Raman microspectrometry, and scanning electron microscopy/energy dispersive X-ray spectrometry. The authors' interest in this combination of compounds stems from their potential use as surrogates for sea spray aerosol within laboratory studies. The authors are correct that existing studies of the NaCl–MgCl₂ are few. However, the relevance of the system studied to sea spray aerosols is limited to only one or two of the mixing ratios they studied. Despite this the manuscript represents a useful contribution to the literature so I advise its publication in ACP following minor revisions.

Response: We thank the reviewer for the positive evaluation of our work and useful comments.

As far as the relevance of studying a wide range of mixing ratios for the NaCl–MgCl₂ system goes, several references are given in the text (Page 17800, Lines 17-27; Page 3, Lines 76-84 in revised text), which report chemical fractionation of nascent sea spray aerosols (SSAs) into NaCl-rich and Mg²⁺-rich or MgCl₂-rich fractions during field studies and in laboratory ocean atmosphere facilities. It is evident from these studies that NaCl and MgCl₂ dominate the phase changes and colligative properties (including viscosity and surface tension) of nascent SSAs. Hence, the elucidation of the hygroscopic behavior and chemical microstructure of NaCl–MgCl₂ is of primary importance to explain more complex nascent SSAs in a better way. Further, the understanding of the hygroscopic behavior of a two component system is incomplete without deriving the full phase diagrams for deliquescence and efflorescence, which demands the study for a wide range of mole fractions including the eutonic composition.

As a final general comment, from the reviewers' perspective it would be useful if the authors could include some discussion on both the relevance of the offline experimental procedures used to atmospheric hydration-dehydration processes, as well as whether the 2-D area ratios that the authors present can be compared to measurements made by "online" measurements e.g. those using Hygroscopic Tandem Differential Mobility Analyzers (HTDMAs). For example, in order to improve models which include sea spray aerosols it would be useful to convert the measured hygroscopic growth to hygroscopic growth factors (usually defined as wet divided by dry diameter assuming a spherical particle).

Response: The conversion of the measured hygroscopic growth to hygroscopic growth factors requires the accurate values for "contact angles" vs. RH of micro-droplets and also the initial mass of solid particles (Eom et al., 2014), which is not feasible to obtain in our experimental set-up. Despite the limitation in comparing the growth factors, the experimentally measured DRH values are compared with the corresponding DRH values calculated from the thermodynamic model AIOMFAC in the deliquescence phase diagram (Figure 7). Regarding the relevance of the offline experimental procedures used to atmospheric humidification-dehydration processes, we think that the work presented here can explicitly show how this offline procedures can perform.

Specific comments from Anonymous referee #1

Manuscript title - In its current form the title is rather confusing. The authors refer to efflorescence during humidifying process. Presumably the authors are referring to the efflorescence they observed within one type of particle at a certain mixing ratio of NaCl-MgCl₂. Given that this effect was only observed under a specific set of conditions (with a Mg⁺² to Na⁺¹ ratio far higher than that of seawater) and that its inclusion makes the title confusing, I suggest the title be simplified to the following "Hygroscopic behavior of NaCl-MgCl₂ mixture particles as nascent sea-spray aerosol surrogates".

Response: Efflorescence during humidification was observed for the first time in laboratorygenerated particles. This observation is one of highlights of this work and provides a fundamental basis for understanding the hygroscopic properties of nebulized pure MgCl₂ and NaCl–MgCl₂ mixture particles more clearly. Throughout the manuscript the authors refer to "humidifying" and "dehydration" modes. I think it is easier for the reader if they are referred to as "hydration" and "dehydration" modes.

Response: Hydration is a term also used for water (in liquid phase) absorption within salt particles. We have replaced the term humidifying by "humidification" (absorption of vapor-phase water into particles/droplets) and retained the term "dehydration" (loss of aqueous-phase water from droplets) in the entire revised manuscript and also Figures 1–6 (Revised Figures are also uploaded with the revised manuscript).

Page 17798 line 1 - The authors refer to the salts NaCl and MgCl2 as "the two major constituents of seawater. . . ". This is not technically correct as any aqueous solution should be thought of as a mixture of ions and not salts. A sentence along the lines of the following would be more accurate: "Alongside Cl^{-1} , Na^{+1} and SO^{-2}_{4} , Mg^{+2} is a major ionic constituent of seawater. Therefore, NaCl-MgCl2 mixture particles might better represent sea-spray aerosols (SSAs) than pure NaCl."

Response: We thank the reviewer for pointing out this error. In the revised manuscript we have revised the sentence as: "As Na⁺, Mg²⁺, and Cl⁻ are major ionic constituents of seawater, NaCl–MgCl₂ mixture particles might represent sea-spray aerosols (SSAs) better than pure NaCl." in the revised text (Page 1, Line 8-9).

Page 17799 line 3 - As above the authors need to be careful not to refer to salts when discussing aqueous solutions such as those of sea spray aerosol droplets. I suggest "For nascent sea spray aerosol, the major ionic constituents are Cl^{-1} , Na^{+1} , SO^{-2}_4 , Mg^{+2} , Ca^{+2} , and K^{+1} .

Response: Incorporated in lines 52-53 of revised text.

Page 17800 line 17 - Suggest rephrase as follows " $MgCl_2$ may play a key role in both the heterogeneous atmospheric chemistry as well as the chemical fractionation of ambient or laboratory-generated SSAs."

Response: Many references cited in the section and atmospheric implications section support our expression. Two more references (Gaston et al., 2011; Ault et al., 2013), which also report the

crucial role of MgCl₂ or Mg²⁺ hydrated ions in nascent SSA properties, are added in the revised manuscript (Lines 78, 669, 671 - Ref.: Lines 798-800 and Line 655 - Ref: Lines 748-751).

Page 17801 line 7 - Suggest rephrase as follows "Therefore, NaCl-MgCl2 mixture particles might better represent the hygroscopic behavior of nascent SSAs".

Response: Rephrased in lines 88-89 of revised text.

Page 17804 line 24 - The authors state that particles larger than 0.5 μ m in 2-D diameter could be analyzed using their optical microscopy setup. However, they state on Line 12 of Page 17803 that particles ranged in size between 1 and 10 μ m. Was it that their atomizer only produced particles larger than 1 μ m or were particles smaller than this simply excluded from the analysis?

Response: The atomizer generates particles or droplets in a much larger size range. Particles larger than 1 µm were analyzed because high quality hygroscopic OM data can be obtained from them. The text has been revised (lines 176–178)

Page 17805 line 5 - Although the authors state that the RH control system used for their Raman microspectrometry measurements was exactly the same as that used for the optical microscopy measurements they state a different reproducibility ($\pm 1.5\%$ for the Raman measurements compared to $\pm 0.5\%$). The authors should explain the reason for this difference.

Response: The different reproducibility was obtained by measuring DRH of pure NaCl using two different hygrometers, i.e. Testo 645 (OM, Page 17804, Line 8; line 163 in revised text) and Testo 635 (RMS, Page 17805, Line 5; line 192 in revised text). The RH control systems are the same for both, but RH readings are different.

Page 17895 line 23 - The authors state that they measured the chemical composition of effloresced particles but do not state what the RH was for these measurements. Given that they show that RH influences the measured particles at RH's below 10% this should be mentioned.

Response: The term, "effloresced particles" implies already solidified particles. We think there's no need to mention RH as SEM/EDX measurements are performed under vacuum.

Page 17808 line 19 - The authors do well to discuss their observations of the formation of $MgCl_2 4H_2O$ rather than the stable crystalline $MgCl_2 6H_2O$ citing that the 2-10 minutes required for their measurements is "insufficient for the thermodynamically predicted but complex crystalline $MgCl_2 6H_2O$ structure to take shape". This seems plausable. In this context it would be nice to know exactly the rate of change of the RH especially given the authors comments that "In real ambient conditions, the RH changes can also be abrupt." As an aside this sentence would read better as "However, it should be noted that under ambient conditions RH changes can be more abrupt."

Response: The RH change rates of 0.3 % per 2 min. for OM and 3.0 % per 10 min. for in-situ RMS are implied from the descriptions in the experimental section: i.e., Page 17804, Line 10 and Page 17805, line 18-20 (lines 178-183, 204-205 in revised text). The expression has been changed as suggested in line 282 in text.

Section 3.2.2 - The observation of three distinct types of particles for these mixing ratios is interesting although rather academic given the high Mg^{+2} to Na^{+1} ratio relative to that of seawater. Given that on page 17816 line 1 the authors state "... the different types of particles are formed somewhat randomly...". I wonder whether the authors observed any differences with particle size? Also, a number of recent studies have highlighted the importance of the particle generation method (e.g. Collins et al., 2014) when generating sea spray aerosol in the laboratory. It would be interesting to compare these atomizer results with different aerosol generation methods to see whether this affects the type of particles formed.

Response: No size correlation was observed for different types of particles, and the different behavior was rather random due to the heterogeneous nucleation for Types B and C particles. These Types B and C as well as Type A were observed when the humidification and dehydration processes were repeated in cycles and also observed in the separate in-situ RMS experiments. Hence, the observation of three types of particles is not related to a certain atomization method. The atomizer which generated aqueous inorganic ionic droplets maintained their respective mixing ratios as in the bulk, which is vindicated by the reproducible second DRHs against the second DRHs calculated theoretically from the AIOMFAC model in the phase diagram (Figure 7).

Therefore in the context of this work, it does not seem necessary to compare this system with other aerosol particle generating systems.

Page 17822 line 22 - Here the authors compare their measurements with those of Tang et al. (1997) which were measured using an electrodynamic balance (EDB). Given this comparison I miss some discussion on how 2-D measurements such as those conducted during this study can be compared to mass based measurements of hygroscopicity such as those obtained using an EDB or electrical mobility based measurements of hygroscopicity such as those obtained using HTDMAs.

Response: Although the growth factors cannot be convertible as stated above, DRHs, ERHs, and hygroscopic curve shapes can be compared, and the similarity between the different data is obvious as given in the text.

Page 17822 line 25 - As the authors state, seawater contains ions apart from Cl^{-1} , Na^{+1} , and Mg^{+2} e.g. SO^{-2}_{4} , Ca^{+2} , and K^{+1} . As such "genuine SSA" does not usually exhibit distinct MDRH or MERH which rather contradicts the authors claim of atmospheric relevance for the XNaCl = 0.9 mixture. In future work it would be useful to see these inorganic species added for comparison.

Response: Although the dominance of NaCl and MgCl₂ (or Cl⁻, Na⁺ and Mg²⁺) in the hygroscopic behavior of inorganic supermicron sea salt particles (or aqueous droplets) were well reported in literature (Schindelholz et al., 2014), the small different behavior of genuine SSA regarding MDRH and MERH should be investigated in the future as suggested by the reviewer.

Page 17823 line 3 - Here the authors state "These observations suggest that pure MgCl₂ species (Fig. 1b) play a strong role in the hygroscopicity of the NaCl-MgCl₂ mixture system as well as the nascent ambient SSAs." I agree that differences in observed hygroscopic growth between pure NaCl particles and NaCl-MgCl₂ mixture particles suggest that MgCl₂ influences the hygroscopicity of the mixture particles. However, it does not say anything about the role of MgCl₂ in nascent sea spray particles since the authors would have had to have studied an inorganic mixture containing SO^{-2}_4 , Ca^{+2} , K^{+1} etc. This sentence should be rephrased to read "These observations suggest that pure MgCl₂ species (Fig. 1b) play a strong role in the hygroscopicity of the NaCl-MgCl₂ mixture system."

Response: MgCl₂ and fresh SSAs were both reported to contain water even at low RH in the references discussed in the introduction (Page 17800) unlike pure NaCl particles. These and the observation of low DRH and ERH due to the MgCl₂·4H₂O-dominant eutonic component in the NaCl-MgCl₂ mixture particles clearly indicate the role of MgCl₂ in nascent SSA hygroscopic properties as well as aqueous phase chemistry. Regarding other inorganic ions (K⁺, Ca²⁺, and SO₄²⁻), they or their potential salts do not exhibit such low DRHs or ERHs.

Page 17823 line 6 - The language should be toned down here for the same reason as above. I suggest: "Mg+2, residing at the particle edges (core-shell type micro-structure, as shown in Fig. 9) and being in an aqueous phase even at very low RHs, i.e., at RHs higher than ~ 15.9 % and ~ 5 % in the hydration (Fig.7) and dehydration (Fig. 8) modes, respectively, may have important implications for nascent SSA heterogeneous chemistry (Wise et al., 2009; Woods et al., 2010, 2012; Liu et al., 2007)."

Response: The "may" is inserted in the revised text (line 653) as suggested.

Page 17823 line 28 - "MgCl2-rich particles can maintain. . . ". This sentence is a repeat of that on line 10 of the same page and should be removed.

Response: The repeated sentence is removed from the revised manuscript.

Technical corrections

Page 17807 line 21 - Should read: ". . . typical for MgCl₂ 4H₂O (Gough et al., 2014) were observed, . . . ".

Response: Corrected in line 256 of revised text.

Page 17813 line 11 - Should read: "For type B particles, three deliquescence transitions and one intermediate efflorescence transition was observed. . .

Response: Original "were" is correct instead of the suggested "was".

Page 17814 line 6 - Should read: "With further decreases in RH, the droplet sizes decreased noticeably at RH = 24.1-23.9 % for Type A particles (Fig. 5a), 25.1-24.9 % for Type B particles (Fig. 5b), and at RH = 24.9-23.9 for Type C particles (Fig. 5c), due to the crystallization of NaCl".

Response: Corrected in lines 423–425 of revised text.

Page 17815 line 17 - Would read better as: "Efflorescence of laboratory generated particles during humidification has not been reported previously."

Response: Corrected in lines 460–461 of revised text.

Page 17815 line 23 - Should read: "As shown in Fig. 6e, the Type C particle effloresced at a higher ERH of 16.8 %...".

Response: Corrected in line 465 of revised text.

Page 17816 line 16 - As above this should read: "... takes place at a higher ERH range of 23.7-11.9 %...".

Response: Corrected in line 485 of revised text.

Page 17817 line 12 - Would read better as: "For XNaCl = 0.05 the frequency with which particles of Type B and C are encountered is much lower (Tab. 1), most likely because the NaCl seeds were smaller. . . "

Response: Corrected in lines 509–510 of revised text.

Page 17818 line 10 - Should read: "Figures 4b and c present the..."

Response: That typesetting was done by ACP.

Page 17821 line 7 - Should read: "To the best of the authors' knowledge, this is the first experimental phase diagram for efflorescence of mixed NaCl-MgCl2 particles."

Response: Corrected in lines 601 and 602 of revised text.

Page 17822 line 4 - Should read: "Figures 9a and b show...".

Response: That typesetting was done by ACP.

Page 17822 line 8 - Should read: ". . . whereas Mg and O (from $MgCl_2 4H_2O$) are more concentrated. . . ".

Response: Corrected in line 628 of revised text.

General Comments from Anonymous referee #2

In Hygroscopic behavior of NaCl–MgCl₂ mixture particles as nascent sea-spray aerosol surrogates and observation of efflorescence during humidifying process, the authors measure water uptake and phase behavior of aqueous droplets containing sodium and magnesium chloride salts. The work is motivated by the need to characterize the hydroscopic behavior of salt systems that represent sea spray aerosol particles better than pure NaCl aqueous systems alone. Measurements are performed using optical microscopy, with supporting characterization with Raman microspectrometry and, for a limited number of cases, X-ray spectrometry.

The aqueous solutions studied include the two pure salt systems, as well as 12 distinct mixed chemical compositions of 0.01 to 0.9 solute mole fraction NaCl, with measurements performed over a 3% to 90% relative humidity range. The amount of experimental characterization is impressive. The only other similar NaCl-MgCl₂-H₂O laboratory single particle study (Chan et al. 2000) is limited to one molar ratio, with a more restricted relative humidity range. In addition to new experimental characterization and comprehensive phase diagrams, the authors also find scientifically interesting results, including a kinetically favored MgCl₂.4H₂O structure in pure MgCl₂ aqueous systems instead of the thermodynamically predicted MgCl₂.6H₂O.

Publication in ACP is recommended, after the authors address the comments below.

Response: We thank the reviewer for the positive evaluation of our work. The responses to the specific comments by the reviewer (italics) are listed below.

Specific comments

- More discussion is needed on if a (quasi-)equilibrium state is truly reached at each RH step change. For levitated single particle studies, an incremental change in the RH value is held until there is no change in mass at that value. Is a similar procedure used here for OM? Is the RH value held until this is no change in area? If not, kinetic artifacts may arise. For example, a rate dependence may explain the reported particle size dependence in during dehydration, with the ERH and MERH RH values lower with larger particles (lines 8-10, p17812).

Response: The steady state (or quasi-equilibrium) is reached in much shorter time than 2 min. which can be clearly confirmed by the sudden morphological and/or size change of particles/droplets responding to the RH change and no further morphological and/or size change after then. Just to make sure the equilibrium state is attained after the RH change, the optical images of an "ensemble of particles" are recorded after 2 min. from each step of RH change. This description is included in the revised version (lines 178–183).

- There is significant structural rearrangement of the particles represented in Figures 3 (0.9 solute mole fraction NaCl) and Figure 5 (0.2 solute mole fraction NaCl). Do these observations of rearrangement occur consistently at the same RH values for all particles of the same composition and type?

Response: When the crystallization of salts within nebulized or effloresced micro-droplets occurs, there may be some lattice defects, which are responsible for structural rearrangements in the lattice prior to the thermodynamic deliquescence transition upon humidification and adsorption of moisture (as mentioned at Lines 16-18, Page 17810 in ACPD paper). Although these rearrangements are more clearly observed for particles in Figures 3 and 5, this kind of rearrangement at RHs just before the prompt deliquescence transition is quite regularly observed for crystalline inorganic salt particles (Ahn et al., 2010).

- Too much attention may have been given to the three particles types in Section 3.2.2, given the overlapping range in critical RH values in both hydration and dehydration behavior for each of

the three types (Figures 7 and 8). Some statistical analysis is needed to convince the reader that there truly are three distinct behaviors observed. If the differences in the three states are robust, more discussion is needed for why these three occur.

Response: Encountering frequencies of the three particle types obtained from 20–40 particles are listed for all the mixing ratios in Table 1. We believe that the substantial encountering frequencies, i.e., 76 % and 63 % of particle Types B + C, observed for the $X_{NaCl} = 0.1$ and 0.2, respectively, need to be recognized by the inclusion of particle Types B and C phase in the phase diagrams (Figures 7 and 8), especially because the phase involves crystallization of MgCl₂·6H₂O (Types B + C) instead of MgCl₂·4H₂O (Type A), while only MgCl₂·4H₂O (Type A) is more frequently crystallized in other mixing ratios.

We think the explanations for observation of the three types are quite explicit and also convincing with both optical images and Raman –OH vibrational signatures (Figures 5 and 6). For the mixing ratios of $X_{\text{NaCl}} = 0.1$ and 0.2, we observed the formation of MgCl₂·6H₂O among particles of Types B and C, and concluded that the kinetic barrier to MgCl₂·6H₂O crystallization can be overcome by heterogeneous nucleation in presence of optimally sized seeds. These findings provide the fundamental basis for understanding the hygroscopic properties of nebulized pure MgCl₂ and NaCl–MgCl2 mixture particles more clearly. Similar heterogeneous nucleation of (NH₄)₂SO₄ in presence of optimally sized kaolinite seeds was reported by Pant et al (2006). A sentence and the above reference is added in revised version (lines 487-488, and Ref: lines 899-901).

- The RH step change is 0.3% in RH for OM, but around 3% in the Raman characterization. Why is the procedure different? If OM is run at 3% step changes to match the procedure used to obtain the spectroscopy results, would the same efflorescence/deliquescence curves result as with 0.3% changes?

Response: In-situ RMS is used as a complementary method here to confirm the hydrate structures of MgCl₂·4H₂O and MgCl₂·6H₂O and corresponding "approximate" DRHs and MDRH of MgCl₂ or MgCl₂-dominant eutonic part only (Figures 2 and 6) and not to obtain accurate and detailed hygroscopic curves which can be obtained by OM.

As already mentioned above, the steady state between ambient water vapor and particle/droplet inside the impactor is established in a much shorter time than 2 min. for recording optical images by OM, while the in-situ Raman spectra were collected over a span of 10 min. (for an ensemble of particles), which is also much longer than the time taken for establishing steady state with 3.0 % RH changes. Hence, there is no doubt that with step changes of RH = 3.0% the deliquescence/efflorescence curves would be the same for OM as well.

- It would be beneficial if the author could connect the area ratio vs. RH results from OM (e.g. Figure 4a) to the more traditional mass fraction solute or mass ratios vs. RH results from EDB experiments (e.g. Fig 1 in Chan et al., 2000).

Response: The conversion of the area ratio into the traditional mass fraction solute or mass ratios requires the accurate values for "contact angles" vs. RH of micro-droplets and also the initial mass of solid particles (Eom et al., 2014), which is not feasible to get in our experimental set-up. Despite the limitation in comparing the growth factors, the experimentally measured DRH values are compared with the corresponding DRH values calculated from the thermodynamic model AIOMFAC in the deliquescence phase diagram (Figure 7).

Technical corrections

- The readability of the manuscript could be improved significantly by fixing run-on paragraphs (e.g. line 5 p17807 to line 20 p17808) and compound sentences.

Response: Paragraph break provided at line 268 and compound sentences revised as far as possible.

- (Line 2, p17830) a space is needed between salts and with

Response: Corrected.

- (Line 16, p17802) Co-efficients should be Coefficients

Response: Corrected.

- (entire manuscript) Use 'hydration' or 'humidification' instead of 'humidifying'

Response: Replaced the term humidifying by "humidification" in the entire revised manuscript and also the revised Figures 1–6.

- (introduction) Use the ion types, instead of electrolyte names, when discussing the sea water composition (note, it was done correctly in lines 16-18, p17822 of section 3.6).

Response: Already incorporated as described in response to Anonymous referee # 1.

Hygroscopic behavior of NaCl-MgCl₂ mixture particles as nascent sea-spray aerosol
 surrogates and observation of efflorescence during humidification

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6

7 ABSTRACT

8 As Na⁺, Mg²⁺, and Cl⁻ are major ionic constituents of seawater, NaCl–MgCl₂ mixture 9 particles might represent sea-spray aerosols (SSAs) better than pure NaCl. However, there have 10 been very few hygroscopic studies of pure MgCl₂ and NaCl-MgCl₂ mixture aerosol particles 11 despite the MgCl₂ moiety playing a major role in the hygroscopic behavior of nascent SSAs. 12 Laboratory-generated pure MgCl₂ and NaCl-MgCl₂ mixture aerosol particles with 12 mixing 13 ratios (0.01 \leq mole fraction of NaCl (X_{NaCl}) \leq 0.9) were examined systematically by optical 14 microscopy (OM), in-situ Raman microspectrometry (RMS), and scanning electron 15 microscopy/energy dispersive X-ray spectrometry (SEM/EDX) elemental X-ray mapping to observe their hygroscopic behavior, derive the experimental phase diagrams, and obtain the 16 17 chemical micro-structures. Dry-deposited MgCl₂·6H₂O particles exhibited a deliquescence relative 18 humidity (DRH) of ~ 33.0 % and an efflorescence RH (ERH) of 10.8–9.1 %, whereas the nebulized 19 pure MgCl₂ and MgCl₂-dominant particles of $X_{NaCl} = 0.026$ (eutonic) and 0.01 showed single-stage transitions at DRH of ~ 15.9 % and ERH of 10.1–3.2 %. The characteristic OH-stretching Raman 20 21 signatures indicated the crystallization of MgCl₂·4H₂O at low RHs, suggesting that the kinetic 22 barrier to MgCl₂·6H₂O crystallization is not overcome in the timescale of the dehydration 23 measurements. The NaCl–MgCl₂ mixture particles of $0.05 \le X_{\text{NaCl}} \le 0.9$ generally showed two-24 stage deliquescence: first at the mutual DRH (MDRH) of ~15.9 %; and second with the complete 25 dissolution of NaCl at the second DRHs depending on the mixing ratios, resulting in a phase 26 diagram composed of three distinct phases. During dehydration, most particles of $0.05 \le X_{\text{NaCl}} \le$ 27 0.9 exhibited two-stage efflorescence: first, by the homogeneous nucleation of NaCl; and second,

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28 at mutual ERH (MERH) of ~ 10.4–2.9 %, by the crystallization of the MgCl₂·4H₂O moiety, also 29 resulting in three distinct phases. Interestingly, particles of $X_{\text{NaCl}} = 0.1$ and 0.2 frequently showed 30 3 different types of mutual deliquescence behaviors. The first type exhibited an MDRH at ~15.9 %. 31 The second exhibited the first MDRH at ~15.9 %, efflorescence to MgCl₂·6H₂O (confirmed by insitu RMS) at RH of ~16.1–25.0 %, and a second MDRH at ~33.0 %. The third showed an MDRH 32 at ~33.0 %. Some particles of $X_{\text{NaCl}} = 0.1$ and 0.2 also exhibited higher MERHs = 15.2–11.9 % and 33 34 23.7–15.3 %, respectively, forming MgCl₂·6H₂O. These observations suggest that the presence of sufficient condensed water and optimally sized crystalline NaCl ($X_{NaCl} = 0.1$ and 0.2) acting as 35 36 heterogeneous nucleation seeds helps overcome the kinetic barrier, leading to the structural growth 37 and crystallization of MgCl₂·6H₂O. SEM/EDX elemental X-ray mapping showed that the 38 effloresced NaCl-rich particles contain homogeneously crystallized NaCl in the center, surrounded 39 by MgCl₂·4H₂O. The observation of an aqueous phase over a wider RH range for NaCl-MgCl₂ 40 mixture particles indicates their more probable heterogeneous chemistry compared to pure NaCl 41 particles as a nascent SSA surrogate.

42

43 INTRODUCTION

44 Sea-salt or sea-spray aerosols (SSAs) are produced from waves through bubble bursting 45 and constitute the second most abundant natural atmospheric aerosols (25-50% of the aerosol mass) 46 after mineral dust particles (Finlayson-Pitts and Pitts, 2000). A study of the hygroscopic behavior 47 of inorganic aerosol particles, closely simulating the chemical compositions of nascent sea-salts, 48 should provide valuable insights into several important SSA properties: (i) aerodynamic properties, 49 (ii) cloud-droplet nucleation efficiency, (iii) optical properties, and (iv) physicochemical changes 50 through complicated heterogeneous chemical reactions with various atmospheric gas-phase 51 species (Meskhidze et al., 2013; King et al., 2012; Tang et al., 1997; Haywood and Boucher, 2000; 52 ten Brink, 1998; Krueger et al., 2003). For nascent SSAs, the major ionic constituents are Cl⁻, Na⁺, 53 SO_4^{2-} , Mg^{2+} , Ca^{2+} , and K^+ (Seinfeld and Pandis, 2006). Because NaCl constitutes ~ 80 % of sea-54 salts by mass, it has long been treated as a nascent SSA surrogate, i.e., the hygroscopic behavior 55 of a single-component NaCl aerosol system has been used to parametrize the thermodynamic and 56 optical properties and cloud activation efficiency of nascent ambient SSAs (Tang et al., 1997; 57 Niedermeier et al., 2008). On the other hand, nascent SSAs can react with gaseous species, such

58 as NO_x and HNO_3/H_2SO_4 , within few minutes to hours of their residence in air (ten Brink, 1998; 59 Saul et al., 2006; Liu et al., 2007). Further, these partially or fully reacted SSAs can interact with 60 volatile organic carbons (VOCs), secondary organic aerosols (SOAs), etc. Previous studies have been performed to explore the hygroscopic properties of these aged SSAs. For example, the 61 62 hygroscopic behavior of laboratory generated aerosol particles of NaCl mixed with dicarboxylic acids (stable water-soluble organics) was reported (Krieger et al., 2012; Ghorai et al., 2014; Ma et 63 64 al., 2013). In addition, it was demonstrated that both airborne and laboratory-generated SSAs are complicated in their chemical characteristics and mixing states (Wise et al., 2007; Wise et al., 2009; 65 Prather et al., 2013). Therefore, the current understanding of the hygroscopic properties of ambient 66 SSAs is "low" as reported in a recent review by Meskhidze et al. (2013). The contributions from 67 other constituents, such as sea-salt (ss)- SO_4^{2-} , non-sea-salt (nss)- SO_4^{2-} , NO_3^{-} , and organics cannot 68 69 be evaluated further unless the hygroscopic behavior of the primary inorganics in nascent SSAs is 70 clearly defined.

71 MgCl₂, the second most abundant constituent of nascent SSAs, plays a key role in 72 heterogeneous atmospheric chemistry as well as chemical fractionation in ambient or laboratory-73 generated SSAs. For example, the uptake of gaseous HNO₃ was claimed to be faster on the 74 NaCl-MgCl₂ mixture particles than on the pure NaCl particles (Saul et al., 2006; Liu et al., 2007); Mg²⁺ and organic species mainly constituted the submicron SSAs generated from a laboratory 75 76 ocean-atmosphere facility, whereas NaCl dominated the supermicron inorganic SSAs (Prather et al., 2013); in marine aerosols, a Mg²⁺-rich chloride moiety was segregated from the NaCl moiety 77 78 (Wise et al., 2007; Gaston et al., 2011); and the SSAs collected at an Antarctic coastal site (Hara 79 et al., 2012) and during the JASE traverse campaign (Hara et al., 2014) were fractionated into Mg-80 rich and NaCl-rich salt particles. In addition, it was reported that laboratory-generated SSAs and pure MgCl₂ contained residual water, even at very low relative humidity (RH) (Cziczo et al., 1997; 81 82 Cziczo and Abbatt, 2000; Tang et al., 1997). The hygroscopic growth factors of ambient or 83 laboratory-generated SSAs plotted as a function of the RH were reported to be different from that 84 of pure NaCl (Tang et al., 1997; Ahn et al., 2010; Schindelholz et al., 2014). This different hygroscopic behavior can affect the cloud droplet nucleation efficiency. For example, the critical 85 86 supersaturation for the cloud droplet nucleation of particles generated from an artificial 87 seawater-oxalic acid mixture was closer to that of NaCl-MgCl₂-oxalic acid mixture particles than that of NaCl-oxalic acid mixture (Drozd et al., 2014). Therefore, NaCl-MgCl₂ mixture particles

89 might better represent the hygroscopic behavior of nascent SSAs.

90 To obtain a better understanding for hygroscopic behavior of the NaCl-MgCl₂ mixture 91 particles, the hygroscopic properties of pure NaCl and MgCl₂ salts need to be understood first. The 92 hygroscopic properties of pure NaCl particles are well established. Briefly, during the 93 humidification process, where RH is changed from low to high, solid NaCl particles at low RH 94 dissolve completely and form aqueous droplets at the deliquescence RH (DRH) of ~75 %. During the dehydration process, where RH is changed from high to low, the concentration of NaCl in the 95 96 aqueous droplets becomes dense as the RH is decreased and NaCl finally crystallizes at its 97 efflorescence RH (ERH) of ~ 45-47 %, which is significantly lower than its DRH (Martin, 2000).

However, there have been few hygroscopic studies of pure MgCl₂ aerosol particles, even 98 99 though the MgCl₂ moiety plays a major role in the hygroscopic behavior of nascent SSAs. 100 MgCl₂·6H₂O is the most thermodynamically stable hydrate of bulk MgCl₂ crystals with a DRH of 101 33 % at room temperature (Lide, 2002). Thus far, only two experiments reported a DRH of ~33 % 102 for aerosol particles nebulized from a MgCl₂·6H₂O aqueous solution (Ha and Chan, 1999; Park et 103 al., 2009). On the other hand, in a flow tube FTIR measurement, it was reported that dry $MgCl_2$ 104 particles began to uptake water at RHs \ll 33%, even though the DRH values were not clearly 105 defined (Cziczo and Abbatt, 2000). Furthermore, just one experiment reported ERH of 14 (±4) % 106 (T = 243 K) for MgCl₂ aerosol particles (Gough et al., 2014). Therefore, the hygroscopic behavior 107 of pure MgCl₂ aerosol particles was examined systematically in this work for the first time.

To the best of the authors' knowledge, there has been no systematic experimental work on the hygroscopic behavior of binary NaCl–MgCl₂ mixture particles. In the only report thus far, for an equimolar mixing ratio of NaCl and MgCl₂, Chan et al. (2000) observed the first ERH at 38 % and calculated a mutual DRH (MDRH) of 32 % and a second DRH of 70 % based on the bulk NaCl–MgCl₂–H₂O system phase diagram (Seidell and Linke, 1965).

In the present study, the hygroscopic behavior, physical states/phases, and microstructures of pure MgCl₂ and NaCl–MgCl₂ mixture particles (covering twelve mixing ratios with NaCl mole fractions ranging from 0.01 to 0.9) were examined by optical microscopy (OM), in-situ Raman microspectrometry (RMS), and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX). The phase transitions of the micrometer sized, laboratory-generated

118 aerosol particles at room temperature were observed by monitoring the size change of the particles 119 in the optical images as a function of the RH. The experimentally measured MDRHs and DRHs 120 were compared with those derived theoretically from the Aerosol Inorganic-Organic Mixtures 121 Functional Activity Coefficients (AIOMFAC) model calculations group 122 (http://www.aiomfac.caltech.edu) (Zuend et al., 2008; Zuend et al., 2011). In-situ RMS was used 123 to observe the phase/structural changes to complement the measurements by OM. SEM/EDX 124 elemental X-ray mapping was used to examine the compositional distribution in effloresced 125 particles. This study systematically describes the full hygroscopic behavior of NaCl–MgCl₂ binary 126 aerosol particles at twelve different mixing ratios.

127

128 2. EXPERIMENTAL SECTION

129 2.1 Preparation of NaCl-MgCl₂ mixture particles

130 Mixed NaCl-MgCl₂ particles were generated by the nebulization of aqueous solutions with 131 different NaCl:MgCl₂ mixing ratios. Pure solutions (1.0 M each) of NaCl and MgCl₂·6H₂O (NaCl, > 99.9% purity, Aldrich; MgCl₂·6H₂O, 99.9% purity, Aldrich) were prepared, and solutions with 132 133 12 different mixing ratios were made by mixing the two solutions volumetrically. A single jet 134 atomizer (HCT4810) was used to generate the aerosol particles to be deposited on the substrates. 135 For all OM observations and most in-situ RMS measurements, the substrate used was Parafilm-M, 136 which is a hydrophobic substrate with a contact angle of $106.8^{\circ} \pm 0.4^{\circ}$ for de-ionized water droplets 137 (Eom et al., 2014). Pure NaCl particles were wet-deposited on the Parafilm-M substrates and their 138 hygroscopic properties were measured to check the accuracy of the experimental set-up. A dry 139 powder or nebulized pure MgCl₂·6H₂O particles and some NaCl-MgCl₂ mixture particles were 140 deposited on a TEM grid and/or Al substrates to perform off-line SEM/EDX measurements after 141 the hygroscopic measurements by OM to avoid charging by the electron-beam on the Parafilm-M 142 substrates. The size of the dry- and wet-deposited particles ranged from 1 to $10 \,\mu m$.

NaCl–MgCl₂ mixture particles with 12 different mixing ratios were investigated, i.e., 11 compositions with NaCl mole fractions of 0.01-0.9 ($X_{NaCl} = 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$, 0.7, 0.8, and 0.9, where X_{NaCl} represents the mole fraction of NaCl.) and a eutonic composition ($X_{NaCl} = 0.026$, which was calculated from the ionic activity products predicted by the AIOMFAC 147 model). Unlike the eutonic compositions of other binary mixture particles, such as NaCl–KCl 148 ($X_{NaCl} = 0.7$) (Li et al., 2014) and NaCl–NaNO₃ ($X_{NaCl} = 0.38$) (Gupta et al., 2015), the 149 NaCl–MgCl₂ mixture system has a MgCl₂-dominant eutonic composition. In the context of 150 thermodynamics, particles with a composition of $X_{NaCl} > 0.026$ were defined as NaCl-rich and 151 those with $X_{NaCl} < 0.026$ were defined as MgCl₂-rich.

152 **2.2 Hygroscopic property measurement**

153 2.2.1 Optical microscopy (OM)

154 The hygroscopic properties of the particles were investigated using a "see-through" inertia 155 impactor apparatus equipped with an optical microscope. The experimental set-up is described in 156 detail elsewhere (Ahn et al., 2010). Briefly, the apparatus was composed of three parts: (A) see-157 through impactor, (B) optical microscope and (C) humidity controlling system. The Parafilm-M 158 substrate onto which the aerosol particles were deposited was mounted on the impaction plate in 159 the see-through impactor. The RH inside the impactor was controlled by mixing dry and wet 160 (saturated with water vapor) N₂ gases. The wet N₂ gas was obtained by bubbling through two 161 deionized water reservoirs. The flow rates of the dry and wet N₂ gases were controlled by mass 162 flow controllers to obtain the desired RH in the range of $\sim 3-90$ %, which was monitored by a digital hygrometer (Testo 645). The digital hygrometer was calibrated using a dew-point 163 164 hygrometer (M2 Plus-RH, GE), providing RH readings of ± 0.5 % reproducibility. The particles 165 on the impaction plate were observed through a nozzle throat using an optical microscope 166 (Olympus, BX51M) equipped with 50x/0.5 numerical aperture objective. The images of particles 167 were recorded by a digital camera (Canon EOS 5D, full frame, Canon EF f/3.5 L macro USM lens) 168 during the humidification (by increasing RH from ~ 3 to 90 %) and dehydration (by decreasing 169 RH from ~ 90 to 3 %) experiments. The image size was 5616×3744 pixels and the image 170 recording condition was set according to the ISO500. The exposure time was 0.4 s and the depth 171 of focus (DOF) was F/3.5. All the hygroscopic experiments were carried out at room temperature 172 $(T = 23 \pm 1 \ ^{\circ}C).$

The changes in particle size with the variation of RH was monitored by measuring the particle areas in the optical images (Ahn et al., 2010). The particle images were processed using image analysis software (Matrox, Inspector v9.0). The size of the imaging pixel was calibrated 176 using 10 μ m Olympus scale bars. Although particles larger than 0.5 μ m in 2-D diameter (D_p) could 177 be analyzed using this system, image fields with particles of 1–10 μ m were selected because high 178 quality hygroscopic OM data can be obtained from them. Each humidity condition was sustained 179 for at least 2 min. A steady state (or quasi-equilibrium) is reached in much shorter time than 2 min 180 which can be clearly confirmed by the sudden morphological and/or size change of 181 particles/droplets responding to the RH change and no further morphological and/or size change 182 thereafter. Just to make sure the equilibrium state is attained after the RH change, the optical image

183 of an "ensemble of particles" was recorded after 2 min from each step of RH change.

184 **2.2.2 In-situ Raman microspectrometry (RMS)**

185 In-situ RMS measurements were carried out under controlled RHs to observe the structural 186 changes in the hydrated water in MgCl₂ crystalline solids. The apparatus is composed of three 187 parts: (A) see-through impactor, (B) Raman microscope/spectrometer and (C) humidity controlling 188 system. The experimental set-up is similar to that used for optical microscopy, with the Raman 189 spectrometer replacing the optical microscope, i.e., the particle impaction and RH controlling 190 system are precisely the same as for the standalone optical microscopy system. The RH was 191 monitored using a digital hygrometer (Testo 635). The digital hygrometer was calibrated using a 192 dew-point hygrometer (M2 Plus-RH, GE), providing RH readings with ±1.5 % reproducibility. 193 The in-situ Raman spectra of the particles deposited on Parafilm-M or Al substrates were recorded 194 using a confocal Raman microspectrometer (XploRA, Horiba Jobin Yvon) equipped with a 50x/0.5 195 numerical aperture objective (Olympus). The optical image size was 908×680 pixels. An 196 excitation laser with a wavelength of 532 nm and 3 mW power was used and the scattered Raman 197 signals were detected using an air cooled multichannel charge-coupled device (CCD) detector. The data acquisition time was 10 s for each measurement. The spectral resolution was 1.8 cm⁻¹. The 198 199 spectra and images were acquired and processed using Labspec6 software.

OM images have a higher spatial resolution (5616×3744 pixels) than the RMS optical images (908×680 pixels), so that they can be processed more accurately for monitoring the 2D size changes and the two measurements were performed separately. Unlike the closely monitored OM images, which were recorded in RH steps of ~0.3 % to generate the 2D area growth curves (Ahn et al., 2010), the Raman spectra of the individual particles were recorded in RH steps of ~3.0 % 205 (~10 min. for an ensemble of particles at each RH) to detect the phase changes and complement206 the OM data.

207 2.3. SEM/EDX elemental X-ray mapping of effloresced particles

208 After the hygroscopicity measurements of the individual particles, SEM/EDX was 209 performed on the effloresced NaCl-MgCl₂ mixture particles to determine the morphology and 210 spatial distribution of the chemical elements (Li et al., 2014; Gupta et al., 2015). The SEM/EDX 211 measurements were carried out using a Jeol JSM-6390 SEM equipped with an Oxford Link SATW 212 ultrathin window EDX detector. The resolution of the detector was 133 eV for Mn Ka X-rays. The 213 X-ray spectra and elemental X-ray maps were recorded using Oxford INCA Energy software. A 214 10 kV accelerating voltage and 0.5 nA beam current was used and the typical measuring times for 215 elemental X-ray mapping were 5 min.

216

217 **3. RESULTS AND DISCUSSION**

218 **3.1 Hygroscopic behavior of pure NaCl and MgCl₂ particles**

Figure 1 shows the 2-D area ratio plots as a function of the RH for the representative wetdeposited NaCl and MgCl₂ particles. The humidification and dehydration curves are represented as the area ratio (A/A_0 : left-hand axis), where the 2-D projected particle area at a given RH (A) is divided by that before starting the humidification process (A_0).

As shown in Fig. 1a, all 26 wet-deposited aerosol particles on an optical image field, which were generated by nebulization from a pure NaCl aqueous solution, showed typical hysteresis curves with DRH of 75.1 (± 0.5) % and ERH of 47.6 – 45.7 %, and these values are consistent with the reported values (Tang et al., 1997; Wise et al., 2007) and previous results (Ahn et al., 2010; Eom et al., 2014).

All 30 wet-deposited aerosol particles nebulized from an 1 M MgCl₂· $6H_2O$ aqueous solution showed a prompt deliquescence transition at DRH of 15.9 (±0.3) % and a distinct efflorescence transition in the RH range of 10.1 - 3.2 % with a mean ERH of 5.9 % (Fig. 1b). At room temperature, thermodynamically stable bulk solids are in the form of MgCl₂· $6H_2O$, which

232 was reported to have a DRH of ~33.0 % (Lide, 2002). On the other hand, the AIOMFAC model 233 predicts its DRH as 36.7 %, which is somewhat biased on the higher side. Until now, just two experiments reported the DRH as \sim 33.0 %, which is similar to the thermodynamic bulk DRH of 234 235 MgCl₂·6H₂O, for aerosol particles nebulized from an MgCl₂·6H₂O aqueous solution despite no 236 ERHs being obtained (Ha and Chan, 1999; Park et al., 2009). On the other hand, in a flow tube 237 FTIR measurement, it was reported that the dry MgCl₂ particles began to uptake water at much 238 lower RHs than 33%, which is similar to the current results, even though the DRH values were not 239 defined (Cziczo and Abbatt, 2000). In addition, they suggested the presence of an MgCl₂ hydrate 240 crystal at RH of < 2%. Until now, no ERH for MgCl₂ aerosol particles has been reported, with the 241 exception of one at T = 243 K, which was 14 (\pm 4) % (Gough et al., 2014).

242 As the observation of a distinct DRH and ERH indicated the presence of a crystalline 243 MgCl₂ hydrate after efflorescence, in-situ RMS measurements of dry-deposited (powdery) and 244 nebulized MgCl₂·6H₂O particles were performed to identify the crystal form of the hydrates. 245 Figure 2 shows optical images and corresponding Raman spectra for a dry-deposited and a nebulized MgCl₂·6H₂O particles, which were recorded during the in-situ RMS measurements. 246 247 During the humidification process, the irregular-shaped powder particle existed as crystalline 248 MgCl₂·6H₂O until RH = 30.6 %, as confirmed by its typical Raman OH stretching signatures $(v(OH) = -3350, 3390, and 3510 \text{ cm}^{-1})$ (Fig. 2a) (Musick et al., 1999; Gough et al., 2014). At RH 249 250 = 34.7%, the powder particle became a round droplet and the OH vibration signal for free water $(v(OH) = -3420 \text{ cm}^{-1})$ was observed, indicating that the deliquescence transition had occurred in 251 the RH range of 30.6 - 34.7 %, which is typical for MgCl₂·6H₂O solids (DRH = 33 %). During 252 253 the dehydration process (Fig. 2b), the aqueous MgCl₂ droplet kept showing a broad free water 254 Raman signal until RH = 15.7 %. At RH = 10.8 %, the optical image showed a morphological change (despite the particle remaining in a round shape), and new OH vibration signals (v(OH) =255 \sim 3405 and \sim 3440 cm⁻¹) typical for MgCl₂4H₂O (Gough et al., 2014) were observed, indicating 256 257 that crystallization had occurred. The particle morphology and Raman signals remained the same 258 when the RH was reduced further to 4.7 %, indicating no change in the crystal structure of the 259 MgCl₂·4H₂O particle. When this MgCl₂·4H₂O particle was subjected to a second humidification 260 process (Fig. 2c), the particles underwent a deliquescence transition at RH of 15.0–16.7 %. This 261 experiment suggests that the MgCl₂·6H₂O powder particles could not return to their original form

once they had been dissolved in the aqueous phase. For a nebulized, wet-deposited MgCl₂ aerosol particle, the RMS measurement results (Fig. 2d and e) indicated that it was crystalline MgCl₂·4H₂O, when dried after wet deposition. The crystalline particle dissolved at RH = 15.5-16.5 % during the humidification process (Fig. 2d). And it crystallized back to MgCl₂·4H₂O at RH = 7.2-6.8 % during the dehydration process (Fig. 2e), which are within the range of phase transition RHs observed by OM.

268 The wet-deposited supermicron $(1-10 \,\mu\text{m})$ aqueous MgCl₂ droplets crystallized at a lower 269 solvated state (MgCl₂·4H₂O) when RH was decreased to \sim 10.1–3.2 % (OM), rather than the stable crystalline MgCl₂·6H₂O. In the observed ERH range of \sim 10.1–3.2 %, the H₂O to Mg²⁺ molar ratio. 270 calculated from the AIOMFAC model (at high supersaturation), was in the range of 5.6–4.1. The 271 272 calculated molar ratio is less than the 6 required for the hexahydrate, but > 4, supporting the observed crystallization as the tetrahydrate. For bulk crystalline MgCl₂·6H₂O, Mg²⁺ ions are 273 solvated first as $[Mg(6H_2O)]^{2+}$ in an octahedral structure and Cl⁻ ions are attached to this hydrate 274 275 (Casillas-Ituarte et al., 2010; Callahan et al., 2010; Hennings et al., 2013). During the dehydration 276 process of MgCl₂ droplets, the rate of the RH change in the measurement time-scale of 2 min for 277 recording each optical image and even 10 min for recording the Raman spectra of an ensemble of 278 particles appears to be insufficient for the thermodynamically predicted but complex crystalline 279 MgCl₂·6H₂O structure to take shape. This indicates the presence of a large kinetic barrier and/or diffusional resistance to the hydrate-ion $[Mg(6H_2O)]^{2+}$ mobilization and nucleation required for 280 the structural growth and crystallization of MgCl₂·6H₂O with decreasing availability of condensed 281 282 water. However, it should be noted that under ambient conditions RH changes can be more abrupt. 283 The thermodynamic properties for the dissolution of different hydrates in MgCl₂·xH₂O (x 284 = 1, 2, 4, 6) at 298 K were reported to have large uncertainties (Wang et al., 1998), even though 285 anhydrous MgCl₂ was predicted to have the same DRH as crystalline MgCl₂·6H₂O at 298 K (Kelly 286 and Wexler, 2005). On the other hand, a higher free energy (less stable) and thus higher solubility 287 for MgCl₂·4H₂O than for MgCl₂·6H₂O can explain the current observation of a lower DRH (15.9 288 (± 0.3) %) for MgCl₂·4H₂O than for MgCl₂·6H₂O (~33 %).

289

290 3.2 Hygroscopic behavior of NaCl-MgCl₂ mixture particles

291 The theoretical aspects of the hygroscopic properties of binary mixture particles are 292 discussed in detail elsewhere (Li et al., 2014; Gupta et al., 2015). In general, for two-component 293 inorganic hygroscopic salt particles, the equilibrium thermodynamics predict two-stage 294 deliquescence and efflorescence transitions. During the humidification process, the first 295 deliquescence transition is due to dissolution of the eutonic component at a mutual DRH (MDRH), 296 which is independent of the mixing ratios; and the second transition due to the complete dissolution 297 of a residual solid component at a second DRH, which depends on the mixing ratio of the two 298 components (Wexler and Seinfeld, 1991). Similarly, during the dehydration process, aqueous 299 droplets with double salts should show stepwise efflorescence transitions; a component of the 300 aqueous droplets precipitates first at their specific ERH depending on their mixing ratio and the 301 remaining aqueous eutonic component effloresces at their mutual ERH (MERH), which should be 302 independent of the mixing ratios. Therefore, effloresced particles can form a heterogeneous, 303 core-shell crystal structure owing to the stepwise crystallization process (Ge et al., 1996). 304 Thermodynamic models, such as the Extended Atmospheric Inorganics Model (E-AIM) 305 (http://www.aim.env.uea.ac.uk/aim/aim.php) (Tang, 1976; Ansari and Pandis, 1999; Carslaw et al., 306 1995; Clegg et al., 1998a, b; Wexler and Clegg, 2002) and the AIOMFAC model 307 (http://www.aiomfac.caltech.edu), can be used to predict the MDRH and second DRHs. On the 308 other hand, as efflorescence is a kinetic or rate-driven process depending on many factors, no 309 general theoretical model that covers the efflorescence of single or multi-component aerosol 310 particles is available (Seinfeld and Pandis, 2006; Cohen et al., 1987; Martin, 2000). Moreover, it 311 was observed that the physical state (i.e., amorphous or crystalline and hydrated or anhydrous 312 nature) of salts plays a vital role in water absorption, diffusion, uptake or dissolution, evaporation, 313 solidification, and morphology changes during the humidification and dehydration processes 314 (Mikhailov et al., 2009). Therefore, the best way to understand the efflorescence behavior of 315 aerosols is through experimental measurements (Seinfeld and Pandis, 2006).

Hygroscopic measurements were performed on 20-40 particles of each mixing ratio of NaCl–MgCl₂ using OM. The hygroscopic behavior of the mixture particles could be divided into three categories, (i) NaCl-rich of $X_{NaCl} \ge 0.3$, (ii) NaCl-rich of $X_{NaCl} = 0.05$, 0.1, and 0.2, and (iii) MgCl₂-dominant particles of $X_{NaCl} = 0.01$ and 0.026 (the eutonic composition), which is discussed in the following sections.

321 **3.2.1 NaCl-rich particles of** $X_{\text{NaCl}} \ge 0.3$

322 During the humidification process, NaCl-MgCl₂ particles with $X_{NaCl} \ge 0.3$ exhibit two 323 stage deliquescence transitions, as is generally expected for binary electrolytic mixture particles. 324 Figure 3 shows the 2-D area ratio plot for the humidification and dehydration processes as a function of the RH for a NaCl-rich particle of $X_{\text{NaCl}} = 0.9$, which is similar to seawater ($X_{\text{NaCl}} =$ 325 0.89) (Lide, 2002), together with the optical images shown at the transition points. Initially at RH 326 327 = 3.1 %, the optical image of the particle clearly shows its angular crystalline nature. During the humidification process, the particle size remains constant until RH = -14 %, where a slight 328 329 decrease in size is observed due to water adsorption at the lattice imperfections of the solid salts 330 in the particle and/or structural rearrangement inside the crystal lattice (Mikhailov et al., 2004; 331 Ahn et al., 2010). A first deliquescence transition was observed from RH = 15.1 to 15.8 %, where the particle morphology changed somewhat at RH = 15.1 %, and the size increased noticeably at 332 333 RH = 15.8 %. With further increases in RH, the partially aqueous particle gradually grew until RH = ~70.0 %, after which a sharp size increase was noted. The optical image at RH = 73.9 % revealed 334 335 a solid inclusion, which completely dissolved to form a homogeneous droplet, with the second 336 transition completing at RH = 74.1 %. Subsequently, with further increases in RH, the aqueous 337 droplet undergoes continuous hygroscopic growth, as shown for the larger droplet at RH = 84.5 %. 338 The first phase transition at RH = 15.8 %, i.e., MDRH of the NaCl-MgCl₂ system, is assigned to 339 the deliquescence of the MgCl₂-dominant eutonic solids in the particle. The observed MDRH 340 deviates from the calculated value of RH = 36.1 % according to the AIOMFAC model; whereas it 341 is comparable to the observed DRH (= 15.9 (± 0.3) %) of crystalline MgCl₂·4H₂O for nebulized 342 pure MgCl₂. At the MDRH, the particle consists of a mixed phase of liquid droplets (eutonic 343 solution) and a NaCl solid inclusion, which is clearly visible in the optical image of the droplet at RH = 73.9 %, just before the complete dissolution of pure NaCl at the second DRH of 74.1 %. The 344 second DRH is consistent with the DRH of 74.1 % observed for a nascent SSA particle levitated 345 346 in an electro-dynamic balance (EDB) by Tang et al.(1997).

The other NaCl-rich particles with compositions of $X_{\text{NaCl}} \ge 0.3$ (e.g., $X_{\text{NaCl}} = 0.5$ in Fig. 4a) also exhibited two-stage phase transitions during the humidification process: the first transition at MDRH (RH = 15.9 (±0.2) %) due to deliquescence of the eutonic component and the second transition due to complete deliquescence of the particles. In the equimolar mixture particles (X_{NaCl} 351 = 0.5, Fig. 4a), the observed second DRH of 67.6 % (on average, 67.3 (± 0.4) %, in terms of 352 reproducibility when the humidification and dehydration processes were repeated) is consistent 353 with the theoretical DRH of 67.5 % calculated using the AIOMFAC model. For an equimolar 354 mixing ratio, Chan et. al. (2000) estimated a MDRH of 32.0 % and a second DRH of 70 % from 355 the phase diagram of the bulk NaCl-MgCl₂-H₂O system. For the NaCl-rich particles with 356 compositions of $X_{\text{NaCl}} \ge 0.3$, the MDRH is independent of the compositions. On the other hand, 357 the second DRHs were dependent on the compositions and shift toward a pure NaCl limit (DRH 358 = 75.1 (± 0.5) %) with increasing NaCl mole fraction, as observed for NaCl-KCl and NaCl-NaNO₃ 359 mixture particles (Li et al., 2014; Gupta et al., 2015).

360 During the dehydration process, the representative NaCl-rich particle of $X_{\text{NaCl}} = 0.9$ (Fig. 3) showed a two-stage phase transition. The liquid droplet decreased gradually in size with 361 362 decreasing RH and became supersaturated with respect to NaCl below RH of 74.1% (DRH for $X_{\text{NaCl}} = 0.9$), where the droplet still appeared to be homogeneous (as shown in the optical image at 363 364 RH = 71.2 %). With the further decreases in RH, the droplet size decreased abruptly at RH = 45.9-45.6 % due to the crystallization of NaCl in the droplet. At RH = 45.6 %, the first ERH for X_{NaCl} = 365 0.9, the particle was composed of a mixed phase of the eutonic solution and NaCl solids, as 366 367 observed clearly from the crystal segments in the optical image. With further decreases in RH, the 368 mixed phase droplet shrank gradually until RH = 5.3-5.1 %, where the MgCl₂-dominant eutonic 369 component in the particle crystallized. At RH = 5.1 % (MERH), a completely effloresced solid 370 particle was formed, which is clearly seen by the reappearance of an overall angular shape and a 371 bright crystalline segment in the optical image (similar to that at RH = 3.1 %, at the start of the humidification process). The measured first ERH and MERH for the particles with a composition 372 of $X_{\text{NaCl}} = 0.9$ vary among the particles, 1–10 µm size, in the same optical image field and are in 373 374 the range, RH = 48.2-45.4 % and RH = 5.6-5.0 %, respectively.

During the dehydration process, the other NaCl-rich particles with compositions of $X_{\text{NaCl}} \ge$ 0.3 also exhibited two-stage phase transitions. For example, for a particle with $X_{\text{NaCl}} = 0.5$ (Fig. 4a), the first transition due to the efflorescence of pure NaCl occurs at RH = 35.5–35.0 % and the second due to the efflorescence of the eutonic component at RH = 5.7–5.5 %. Chan et al. (2000) reported the first ERH of 38 % (within the range of the first ERHs of 40.5–35.0 % observed in this study for 38 particles), but no MERH (in this work, it was observed in the RH range of 6.9–5.0 %), 381 when they performed the dehydration experiments on a single levitated aqueous droplet of 382 NaCl-MgCl₂ with an equimolar mixing ratio ($X_{NaCl} = 0.5$) in an EDB. The first ERHs for the NaCl-383 rich mixture particles with compositions of $X_{\text{NaCl}} \ge 0.3$ are dependent on the compositions and shift 384 toward the pure NaCl limit (ERH = 47.6-45.7 %) with increasing NaCl mole fraction, as observed 385 for NaCl-KCl and NaCl-NaNO₃ mixture particles (Li et al., 2014; Gupta et al., 2015); whereas the 386 MERH, like their MDRH, is almost independent of the particle compositions. The MERHs, 387 however, were observed over a wide RH range (RH = 10.4-2.9 %) due to the stochastic nature of 388 nucleation leading to efflorescence.

389 **3.2.2** NaCl-rich particles of $X_{\text{NaCl}} = 0.05, 0.1, \text{ and } 0.2$

390 In the case of NaCl-rich particles with compositions of $X_{\text{NaCl}} = 0.1$ and 0.2, three types of 391 particles showing 2- or 3-stage deliquescence transitions were observed. Figure 5a-c show the 392 hygroscopic behavior of representative "Types A, B, and C" particles, respectively, where their 393 particle/droplet optical images are also shown at each transition point. During the humidification 394 process, a Type A particle of $X_{\text{NaCl}} = 0.2$ (Fig. 5a) showed an initial small decrease in size due to structural rearrangement before the first deliquescence transition at RH = 15.5-15.8 %. At its 395 396 MDRH of 15.8 %, bright solids in the particle disappeared due to dissolution of the eutonic 397 component. With further increases in RH, it gradually grew until RH = 56.7 %, after which an 398 abrupt increase in size was observed with the dissolution of pure NaCl, i.e., the second 399 deliquescence transition completing at RH of 57.0 % (resulting in a homogeneous droplet in the 400 optical image).

401 For Type B particles, three deliquescence transitions and one intermediate efflorescence 402 transition were observed during the humidification process (e.g., Fig. 5b). Figure 5b shows that 403 the particle size remained constant until $RH = \sim 15.5 \%$, and then underwent an abrupt first mutual 404 deliquescence transition at RH of 15.5–15.8 % (called MDRH₁). The particle grew gradually until 405 the RH reached 21.9 %. Subsequently, an efflorescence-like transition with a decrease in size and a bright, crystallized solid particle were observed at RHs of 21.9–24.9 % and 24.9 %, respectively. 406 Thereafter, the size of the Type B particle remained almost constant until RH = 31.0 %, which was 407 followed by a small decrease in size (structural rearrangement) at RH = 32.0 % and then by a 408 second mutual deliquescence transition at RH = 32.3 - 33.0 % (MDRH₂). The observed MDRH₂ of 409

410 33.0 % for the Type B particle is attributed to the complete dissolution of the crystalline 411 MgCl₂·6H₂O-dominant eutonic part. With further increases in RH, the size of the Type B particle 412 increased gradually until the third deliquescence transition with the dissolution of pure NaCl (NaCl 413 solid inclusion in the optical image at RH = 56.7 % disappears in the optical image at RH = 57.0 %), 414 which occurs at RH of 56.7–57.0 %, similar to the Type A particle (Fig. 5a). The Type C particle (Fig. 5c) did not show the first deliquescence transition at RH of ~ 15.8 % (seen in Fig. 5a and b) 415 416 or recrystallization (seen in Fig. 5b), but its size remained unchanged until RH = 31.0 %, followed 417 by a small decrease in size due to the structural rearrangement at RH = 32.0 %, and a sharp increase 418 in size from RH = 32.3 - 33.0 %, which is the first deliquescence transition or MDRH. The second 419 deliquescence transition was observed as usual at RH = 56.7 - 57.0 %.

420 During the dehydration process, the NaCl-rich particles of $X_{\text{NaCl}} = 0.2$ of Types A-C 421 particles showed two-stage phase transitions (Fig. 5a-c). The liquid droplets decreased gradually 422 in size with decreasing RH and became supersaturated with NaCl below RH = 57.0 % (DRH for 423 $X_{\text{NaCl}} = 0.2$). With further decreases in RH, the droplet sizes decreased noticeably at RH = 24.1-23.9 % for Type A particles (Fig. 5a), RH = 25.1-24.9 % for Type B particles (Fig. 5b), and 424 RH = 24.9 - 23.9 % for Type C particles (Fig. 5c), due to the crystallization of NaCl. At the first 425 426 ERHs of 23.9, 24.9, and 23.9 %, the partially aqueous Types A-C particles, respectively, are 427 composed of a mixed phase of a eutonic solution and NaCl solid. With further decreases in RH, 428 Types A and B droplets gradually shrank until the final perceptible decreases in sizes were 429 observed at RH = 6.1-5.2 % (Fig. 5a) and at RH = 5.4-5.2 % (Fig. 5b), where completely 430 effloresced Types A and B solid particles, respectively, were formed. Their low MERH of 5.2 % 431 suggests that the MgCl₂:4H₂O-dominant eutonic component was crystallized for the Types A and 432 B particles. For the Type C particle, complete efflorescence occurred at RH = 23.9 - 23.7 % with a MERH of 23.7 % (Fig. 5c). The high MERH suggests that the MgCl₂-dominant eutonic part 433 434 crystallized heterogeneously as the MgCl₂·6H₂O moiety on crystalline NaCl seeds, leading to the observed MDRH of ~ 33.0 % for the Type C particle. 435

To clearly explain the above observations, particles with a composition of $X_{\text{NaCl}} = 0.2$ sitting on a Parafilm-M substrate were examined using in-situ RMS. Figure 6 shows the Raman spectra and corresponding optical images, which were recorded during the in-situ RMS measurements of particles of $X_{\text{NaCl}} = 0.2$. As shown in Fig. 6a, at RH = 4.5 %, the Type A particle appears irregular and shows a typical –OH stretching signature for crystalline MgCl₂·4H₂O. At RH = 16.6 %, the Type A particle becomes round-shaped and the broad –OH stretching peak for free-water indicates that it is deliquesced. During the dehydration process, as shown in Fig. 6b, the Type A round droplet at RH = 10.7 % becomes irregular-shaped, i.e., effloresces at RH = 7.6 %, forming a crystalline MgCl₂·4H₂O-dominant eutonic phase. For Type A particles, the NaCl and MgCl₂·4H₂Odominant eutonic solids are dissolved and formed during the humidification and dehydration processes.

447 As shown in Fig. 6c, during the humidification process, the Type B particle appears 448 irregular at low RH (= 4.6 %) and shows a –OH stretching signature for crystalline MgCl₂·4H₂O. 449 At RH = 16.4 %, the particle becomes round and the broad –OH stretching signal for free water 450 indicates that it is deliquesced. With a small increase in RH (to ~ 16.6 %), however, the Type B 451 particle changes its morphology and shows the typical –OH vibration signatures for crystalline MgCl₂·6H₂O, indicating the occurrence of efflorescence. At RH = 33.9 %, the Type B particle 452 453 appears round and shows a free water -OH peak again, indicating that further deliquescence occurs 454 below RH = 33.9 %. During the dehydration process, as shown in Fig. 6d, the Type B round droplet 455 at RH = 15.3 % becomes irregular-shaped, i.e., effloresces at RH = 10.1 %, forming a crystalline 456 MgCl₂ 4H₂O-dominant eutonic phase. For Type B particles, NaCl and MgCl₂ 4H₂O-dominant 457 eutonic solids are formed during the dehydration process, and despite the MgCl₂·4H₂O-dominant 458 eutonic solids being dissolved, the MgCl₂·6H₂O-dominant eutonic solids are formed through 459 efflorescence and are dissolved, and finally, the NaCl solids deliquesce during the humidification 460 process. Efflorescence of laboratory-generated particles during humidification has not been reported previously. 461

As shown in Fig. 6f, at RH = 4.5 %, a Type C particle appears irregular and crystalline and 462 463 shows the typical –OH stretching signature for crystalline MgCl₂· $6H_2O$. At RH = 34.1 %, the Type 464 C particle appears round and shows a free water –OH peak, indicating that deliquescence occurs 465 below RH = 34.1 %. As shown in Fig. 6e, the Type C particle effloresced at a higher ERH of 16.8 % 466 and shows a typical –OH stretching signature for crystalline MgCl₂·6H₂O. For the Type C particles, 467 NaCl and MgCl₂6H₂O-containing crystals are formed and dissolved during the dehydration and 468 humidification processes, as clearly confirmed by the OM and in-situ RMS measurements. On the 469 other hand, this Type C particle does not form MgCl₂·6H₂O again at the next dehydration process,

as shown in Fig. 6g, indicating that this particle is no longer Type C and the different types of
particles are formed somewhat randomly because efflorescence is a kinetic or rate-driven process
depending on many factors.

Table 1 shows the encountering frequencies of Types A-C particles at various NaCl-MgCl₂ mixing ratios in their respective OM experiments. For all mixing ratios except $X_{NaCl} = 0.1$ and 0.2, Type A particles, which form a crystalline MgCl₂·4H₂O-dominant eutonic phase at MERH, are dominant. Owing to the decreasing availability of condensed water during dehydration, large kinetic barrier and/or diffusional resistance for hydrate-ion nucleation make the formation of the crystalline MgCl₂·6H₂O structure difficult, which is already discussed for the nebulized pure MgCl₂ aerosols.

480 For particles of $X_{\text{NaCl}} = 0.1$ and 0.2, the encountering frequencies of the Type B particles 481 are 29 % and 45 %, respectively, and Type C are 47 % and 18 %, respectively, indicating that the 482 formation of MgCl₂·6H₂O-containing crystals is easier at these mixing ratios. Aqueous moieties 483 in particles were reported to effloresce more easily by heterogeneous nucleation in the presence of 484 seeds (Schlenker and Martin, 2005; Li et al., 2014; Gupta et al., 2015). For Type C particles, the crystallization of MgCl₂·6H₂O takes place at an ERH range of 23.7–11.9 % during dehydration 485 (e.g., see Fig. 5c), suggesting that the NaCl crystals of an optimal size ($X_{NaCl} = 0.1$ and 0.2) can act 486 487 as seeds for the heterogeneous nucleation of MgCl₂·6H₂O. Heterogeneous nucleation of 488 $(NH_4)_2SO_4$ in presence of optimally sized kaolinite seeds was also reported by Pant et al (2006). 489 On the other hand, the heterogeneous efflorescence of MgCl₂·6H₂O is also observed during the 490 humidification process for Type B particles (Fig. 5b). Efflorescence during the humidification 491 process was once reported for Amazonian rain-forest aerosols (Pöhlker et al., 2014), where it was claimed that the impacted ambient organic-inorganic mixed aerosols initially had amorphous or 492 493 poly-crystalline structures and underwent restructuring through kinetic water and ion mobilization, 494 resulting in the crystallization of inorganic salts during hydration. During the humidification 495 process, the MgCl₂ 4H₂O-dominant eutonic solids in the effloresced Type B particles of X_{NaCl} = 496 0.1 and 0.2 dissolve at MDRH₁ (= 15.9 (\pm 0.3) %) and some moisture is also adsorbed on the surface of the crystalline NaCl moiety. The $[Mg(6H_2O)]^{2+}$ hydrate-ions appear to be mobilized in 497 the presence of sufficient condensed water at the observed ERH range of $\sim 16.1-24.9$ % during 498 499 hydration ($\sim 23.7 - 11.9$ % during dehydration) and the kinetic barrier is overcome by heterogeneous

nucleation on the optimally-sized NaCl seeds, leading to structural growth and crystallization of the MgCl₂·6H₂O moiety. Therefore, particles of $X_{NaCl} = 0.1$ and 0.2 frequently show a characteristic MDRH of ~ 33.0 (±0.5) % for the dissolution of the MgCl₂·6H₂O-dominant eutonic solids. On the other hand, the crystalline NaCl seeds for the particles of $X_{NaCl} \ge 0.3$, being larger than the optimal size, appear to inhibit the smooth diffusion of water kinetically, which is a primary requirement for the nucleation of [Mg(6H₂O)]²⁺. Therefore, for particles of $X_{NaCl} \ge 0.3$, crystalline MgCl₂·6H₂O is not formed in the timescale of the measurements.

In the case of particles of $X_{\text{NaCl}} = 0.05$, two-stage deliquescence transitions for Type A particles were mainly observed: mutual deliquescence occurring at MDRH of 16.0 (±0.3) % and the second DRH for the remnant NaCl at RH of 40.5 (±1.5) %. For $X_{\text{NaCl}} = 0.05$, the frequency with which particles of Types B and C were encountered was much lower (Table 1), most likely because the NaCl seeds were smaller than the optimal size.

For the NaCl-rich particles of $X_{\text{NaCl}} = 0.05, 0.1$, and 0.2, the second DRHs were dependent 512 513 on the compositions and shifted toward the pure NaCl limit (DRH= $75.1 (\pm 0.5) \%$) with increasing 514 NaCl mole fraction. Figure 7 plots the measured DRHs for the NaCl-rich particles with various 515 compositions as a function of the NaCl mole fraction, showing that the experimental second DRH 516 values are in good agreement with the values calculated from the AIOMFAC model. On the other hand, the observed MDRH (= $15.9 (\pm 0.3) \%$) for Type A particles deviates from that predicted by 517 518 the thermodynamic considerations in the model. In contrast, the observed MDRH₂ for the Type B 519 particles and MDRH for the Type C particle of 33.0 (± 0.5) % agree with the predicted DRH for 520 MgCl₂·6H₂O.

521 In the case of $X_{\text{NaCl}} = 0.2$, the measured first ERH and MERH vary among Types A and B 522 particles, $1-10 \mu m$ in size, on the same optical image field and are in the range of RH = 27.1-523 23.9% (average first ERH = 25.0%) and RH = 10.2-5.2% (average MERH = 7.1%), respectively. 524 In contrast, the Type C particles exhibit MERH in the range of 23.7-15.3 % (average MERH = 525 18.1 %). For Types A and B particles of $X_{\text{NaCl}} = 0.1$, the measured first ERH and MERH vary in 526 the range of RH = 17.4-12.4 % (average first ERH = 15.8 %) and RH = 9.4-6.5 % (average MERH 527 = 7.2 %), respectively, whereas the Type C particles exhibit MERH in the range of 15.2-11.9 % (average MERH = 13.3 %). In the case of X_{NaCl} = 0.05, the measured first ERH and MERH vary 528 529 in the range of RH = 15.5-13.0 % (average first ERH = 13.2 %) and RH = 9.3-6.5 % (average

530 MERH = 6.9 %), respectively. Figure 8 shows the measured ERHs for the NaCl-rich particles with 531 various compositions as a function of the NaCl mole fraction.

532 **3.2.3** MgCl₂-dominant particles of $X_{NaCl} = 0.01$ and 0.026 (the eutonic composition)

Figure 4b and c presents the 2-D area ratio plots for the MgCl₂-dominant particles with the 533 534 eutonic composition ($X_{\text{NaCl}} = 0.026$) and of $X_{\text{NaCl}} = 0.01$ as a function of RH. During the 535 humidification process, the particles of $X_{\text{NaCl}} = 0.026$ and 0.01 show single-stage deliquescence 536 phase transitions from RH = 15.7 to 16.1 % and from RH = 15.6 to 16.1 %, respectively. With 537 further increases in RH, the particles showed continuous and gradual hygroscopic growth. During 538 the dehydration process, the particles of $X_{\text{NaCl}} = 0.026$ and 0.01 decreased gradually in size until 539 they exhibited hysteresis with single-stage efflorescence transitions from RH = 5.3 to 4.5 % and 540 from RH = 4.8 to 4.6 %, respectively. Therefore, the hygroscopic behavior of these particles with 541 MgCl₂-dominant compositions is similar to that of the nebulized pure MgCl₂ particles (Fig. 1b).

The probability of forming a crystalline MgCl₂· $6H_2O$ structure for particles of $X_{NaCl} = 0.026$ and 0.01 is quite low (Table 1), due to the low probability of heterogeneous nucleation in the absence of optimally-sized seeds, as explained above for the case of $X_{NaCl} = 0.05$. NaCl, which is mostly in the aqueous phase, cannot act as a crystalline seeds for heterogeneous nucleation at low RHs, or the sizes of those NaCl seeds are too small for heterogeneous nucleation leading to the formation of a hexahydrate (MgCl₂· $6H_2O$) structure.

548 **3.3 Deliquescence phase diagram of mixed NaCl-MgCl2 particles**

Figure 7 presents the measured first or second MDRHs (MDRH₁ or MDRH₂) and second DRHs of the NaCl–MgCl₂ mixture particles with different mole fractions along with the measured DRHs of the pure NaCl and MgCl₂ particles. As shown in Fig. 7, a clearly demarked phase diagram depicting their deliquescence behavior was obtained experimentally for the first time, for which, until now, there was no experimental data to the best of the authors' knowledge;

- NaCl(s) + MgCl₂(s) phase: both NaCl and MgCl₂ are mixed as solids below the MDRHs
 at all mole fractions;
- 556 2. NaCl(s) + eutonic(aq) phase: a mixed phase of solid NaCl and aqueous eutonic components 557 between the MDRHs and second DRHs for $X_{NaCl} > 0.026$;

3. NaCl(aq) + MgCl₂(aq) phase: both NaCl and MgCl₂ are mixed in the aqueous phase above the second DRHs at all mole fractions.

560 The second DRHs obtained experimentally agree well with the values calculated from the ionic 561 activity products of the constituents predicted by the AIOMFAC model, as shown in Fig. 7 (dashdotted curve for the second DRHs). On the other hand, the observed MDRH₁ (= $15.9 \pm 0.3 \%$) 562 for most particles (of all mole fractions) was lower than the MDRH values of 36.1 % calculated 563 from the AIOMFAC model and 32.0 % estimated using the bulk NaCl-MgCl₂-H₂O system phase 564 565 diagram (Tang, 1976; Chan et al., 2000). This is similar to the case observed for the nebulized pure MgCl₂. On the other hand, particles with compositions of $X_{NaCl} = 0.1$ and 0.2 frequently show two 566 MDRHs at 15.9 (±0.3) % (MDRH₁) and 33.0 (±0.5) % (MDRH₂). The dense ($0.1 \le X_{\text{NaCl}} \le 0.2$) 567 and light $(0.01 \le X_{\text{NaCl}} \le 0.05)$ brown shaded patterns in Fig. 7 indicate the high and low 568 569 frequencies for encountering MDRH₂, respectively (Table 1). The eutonic composition (X_{NaCl} = 570 0.026), which was calculated theoretically from the AIOMFAC model, cannot be ascertained 571 clearly from the experimental data as the deliquescence transition for these MgCl₂-dominant compositions (Fig. 4b and c) becomes similar to that of the nebulized pure MgCl₂ (Fig. 1b). On 572 the other hand, it should be close to the value of $X_{\text{NaCl}} = 0.029$ (NaCl = ~ 1% and MgCl₂ = ~ 35 %) 573 574 calculated from the phase diagram for the bulk NaCl-MgCl₂-H₂O system at 298.15 K based on 575 equilibrium thermodynamics (Seidell and Linke, 1965; Tang, 1976). Chan et al. (2000) calculated 576 a MDRH of 32.0 % and a second DRH of 70 % for an equimolar mixing ratio from the bulk NaCl-MgCl₂-H₂O system phase diagram (Seidell and Linke, 1965), but no experimental DRHs 577 578 were reported.

579 All the mixed NaCl-MgCl₂ particles showed the first deliquescence transition at the 580 MDRH₁ (= 15.9 (± 0.3) %), regardless of the mixing ratio of the two salts, except for compositions 581 of $0.01 \le X_{\text{NaCl}} \le 0.2$, particularly $X_{\text{NaCl}} = 0.1$ and 0.2, where Types B and C particles also exhibited 582 a partial deliquescence transition at MDRH₂ (= 33.0 (± 0.5) %) for the crystalline MgCl₂·6H₂O-583 dominant eutonic components. Thermodynamically, as the first deliquescence transition of mixed-584 salts is governed by the water activity at the eutonic point, the MDRH of the mixed-salt particles 585 is normally independent of the initial composition of the mixture. For the NaCl-rich particles of 586 $X_{\text{NaCl}} > 0.026$, which contain more NaCl than the eutonic composition, as the NaCl mole fraction

increases, the second DRH values approach the DRH of the pure NaCl salt. This suggests that for particles with $X_{\text{NaCl}} > 0.026$, the second-stage deliquescence is driven purely by the solid NaCl remaining after deliquescence of the eutonic composition (Li et al., 2014; Gupta et al., 2015).

590 3.4 Efflorescence phase diagram of mixed NaCl-MgCl₂ particles

591 Figure 8 shows the measured ERHs and MERHs for mixed NaCl–MgCl₂ particles with 592 various mixing ratios as a function of the NaCl mole fraction. Similar to the deliquescence phase 593 diagram, which showed three systematic phases, the efflorescence phase diagram is also composed 594 of three distinct phases:

- NaCl(aq) + MgCl₂(aq) phase: both NaCl and MgCl₂ are mixed in the aqueous phase above
 the first ERHs at all mixing ratios;
- 597 2. NaCl(s) + eutonic(aq) phase: a mixed phase of solid NaCl and aqueous eutonic components 598 between the first ERH and second ERH (MERH) for $X_{\text{NaCl}} > 0.026$; and
- 599 3. NaCl(s) + MgCl₂(s) phase: both NaCl and MgCl₂ are mixed as solids below the second 600 ERH (MERH) for $X_{NaCl} > 0.026$ and below the first ERHs for $X_{NaCl} \le 0.026$.

601 To the best of the authors' knowledge, this is the first experimental phase diagram for 602 efflorescence of mixed NaCl–MgCl₂ particles. The first ERHs of NaCl-rich droplets ($X_{NaCl} > 0.026$) shift toward the pure NaCl limit (RH = 47.6 - 45.7 %) with increasing NaCl mole fraction (see 603 604 Fig. 8). This suggests that the first-stage efflorescence for particles of $X_{\text{NaCl}} > 0.026$ is driven purely by the homogeneous nucleation of NaCl, the rate of which increases with increasing NaCl mole 605 606 fraction (Gupta et al., 2015). Chan et al. (2000) reported that the first ERH for the crystallization 607 of pure NaCl is 38.0 % for an equimolar mixing ratio, which is within the range of the first ERH of 40.3 – 35.0 % (Figs. 4a and 8) measured for the same mixing ratio in the present work. Although 608 609 they did not report MERH, MERHs were clearly observed in this study. For Types A and B 610 particles, the measured MERH₁ were observed over a wide range ($\sim 10.4-2.9$ %) because of the 611 stochastic nucleation events leading to the crystallization of MgCl₂·4H₂O moieties. The MERH₁ 612 range is similar to that for the nebulized pure MgCl₂ particles (ERH = 10.1-3.2 %). On the other 613 hand, MERH₂ values for Type C particles of $X_{\text{NaCl}} = 0.1$ and 0.2 were in the ranges of ~15.2–11.9 % 614 and ~23.7-15.3 %, which is just below their first ERHs of ~17.4-12.4 % and ~27.1-23.9 %,

respectively, because the optimally-sized NaCl seeds, which are needed to facilitate heterogeneous nucleation leading to the crystallization of MgCl₂·6H₂O, are available immediately after the first efflorescence transitions. The droplets with MgCl₂-dominant compositions, such as $X_{NaCl} = 0.026$ and 0.01, showed the single efflorescence transitions over an ERH range of 9.7–3.4 % and 6.2– 4.0 %, respectively.

620

621 3.5 Spatial distribution of effloresced NaCl- MgCl₂ solid particles

622 SEM/EDX was used to examine the morphology and spatial distribution of the chemical 623 components in the effloresced NaCl-MgCl₂ solid particles at various mixing ratios after the 624 humidification and dehydration cycles. Figure 9A and B shows elemental X-ray mapping images 625 for Na, Mg, O, and Na/Mg (mixed) and a secondary electron image (SEI) of NaCl-rich particles with $X_{\text{NaCl}} = 0.9$ (seawater-like mixing ratio) and $X_{\text{NaCl}} = 0.6$, respectively. The elemental X-ray 626 maps in both cases suggest that Na (from NaCl) is concentrated in the central part, whereas Mg 627 628 and O (from MgCl₂·4H₂O) are more concentrated at the edges. This suggests that NaCl nucleates 629 homogeneously to crystallize in the center at the first ERH, whereas the MgCl₂·4H₂O-dominant 630 eutonic phase solidifies on these central NaCl seeds at the second ERH (MERH), corroborating 631 the efflorescence mechanism observed by OM. MgCl2-rich or MgCl2-dominant particles were not 632 shown because MgCl₂ covers whole particles without a visible NaCl moiety and their hygroscopic 633 behavior is similar to that of the nebulized pure MgCl₂ particles.

634 **3.6 Atmospheric implications**

Because Cl⁻ is the most abundant anion, and Na⁺ and Mg²⁺ are the first and second most 635 abundant cationic species, respectively, in nascent sea-salt (Seinfeld and Pandis, 2006), 636 637 NaCl-MgCl₂ binary mixture particles can be good surrogates for the nascently generated 638 inorganic-rich supermicron SSAs. For particles with an approximately seawater-like mixing ratio of $X_{\text{NaCl}} = 0.9$, the hygroscopic curve (2-D area ratio plots as a function of RH, as shown in Fig. 3) 639 640 is similar to those obtained by OM for the particles nebulized from artificial seawater 641 (Schindelholz et al., 2014) and by EDB measurements on sea-salt particles generated from filtered seawater (Tang et al., 1997). In addition, the hygroscopic curve for particles of $X_{\text{NaCl}} = 0.9$ is similar 642 to that obtained for genuine ambient SSAs (Ahn et al., 2010), except that the real genuine SSAs, 643

having other minor chemical species, such as Ca^{2+} , K^+ , SO_4^{2-} , and organics, did not show distinct MDRH or MERH, as observed in this study for the case of $X_{NaCl} = 0.9$. On the other hand, the hygroscopic behavior and growth curve in Fig.e 3 deviated considerably from that of pure NaCl particles, as shown in Fig. 1a and by previous reports (Tang et al., 1997; Ahn et al., 2010; Schindelholz et al., 2014). These observations suggest that pure MgCl₂ species (Fig. 1b) plays a strong role in the hygroscopicity of the NaCl–MgCl₂ mixture system as well as the nascent ambient SSAs.

 Mg^{2+} , residing at the edges (core-shell type micro-structure, as shown in Fig. 9) and being 651 in an aqueous phase even at very low RHs, i.e., at RHs higher than ~ 15.9 % and ~ 5 % in the 652 humidification (Fig. 7) and dehydration (Fig. 8) modes, respectively, may have important 653 654 implications for nascent SSA heterogeneous chemistry (Wise et al., 2009; Woods et al., 2010; 655 Woods et al., 2012; Liu et al., 2007; Ault et al., 2013). As NaCl–MgCl₂ binary mixture particles 656 can maintain an aqueous phase over a much broader RH range than pure NaCl particles, they will 657 be increasingly susceptible to reactions with gas phase inorganic and organic species, such as NO_x, 658 SO_x, HNO₃/H₂SO₄, and dicarboxylic acids (DCAs). Liu et al. (2007) reported the faster uptake of gaseous HNO₃ into NaCl-MgCl₂ mixture particles with a seawater-like mixing ratio and ambient 659 660 SSAs than into pure NaCl particles. The lack of knowledge, however, of the hygroscopic behavior 661 and phases of NaCl-MgCl₂ mixture particles has resulted in large uncertainties for the 662 determination of the uptake coefficient of HNO₃. Therefore, in terms of the aqueous phase 663 chemistry of nascent SSAs, the hygroscopic behavior of NaCl-MgCl₂ mixture particles, systematically investigated in this study for the first time, is of higher relevance as nascent SSA 664 665 surrogates than pure NaCl particles.

The NaCl moiety, crystallizing easily at higher RHs than $MgCl_2$, and the aqueous Mg^{2+} 666 667 moiety, having a high surface tension and viscosity, may have a tendency to separate or fractionate 668 in ambient SSAs. These chemical fractionations can occur even during wave breaking or bubble 669 bursting processes on the sea surface (Keene et al., 2007) and due to high wind speeds (Gaston et 670 al., 2011). Therefore, fractionated NaCl-rich and MgCl₂-rich particles have often been reported for 671 ambient SSAs (Wise et al., 2007; Ahn et al., 2010; Gaston et al., 2011; Hara et al., 2014; Prather 672 et al., 2013). Both ambient and laboratory-generated SSAs show that organic species are mostly associated with Mg-rich inorganics (Keene et al., 2007; Prather et al., 2013). The unexpectedly 673

674 low MDRH and MERH of MgCl₂·4H₂O moiety and the stochastic nature of heterogeneous 675 nucleation for MgCl₂·6H₂O formation in the presence of optimally-sized seeds, together with the 676 presence of organics, may partially explain the intriguing hygroscopic behavior of SSAs 677 (Meskhidze et al., 2013). The heterogeneous crystallization of MgCl₂·6H₂O can also take place in 678 the presence of other seeds in SSAs, such as easily crystallizing $CaSO_4$ (ERH = 80–90 %) (Xiao 679 et al., 2008). Therefore, the hygroscopic properties of all mixing ratios of the NaCl-MgCl₂ system 680 covered in this study, including the MgCl₂-rich/dominant particles, can provide some insight into 681 the physico-chemical characteristics and atmospheric chemistry of nascent SSAs.

682

683 4. CONCLUSIONS

684 The hygroscopic properties, physical states/phases and chemical micro-structures of pure 685 MgCl₂ particles and the two-component NaCl–MgCl₂ mixture particles deposited on substrates 686 were studied by OM, in-situ RMS, and SEM/EDX elemental X-ray mapping. The DRHs and ERHs 687 of laboratory-generated aerosol particles of 1-10 µm size at room temperature were determined by 688 monitoring the 2-D area change for particles on optical images with RH variations between ~3 and 689 90 %. During the humidification process, wet-deposited particles from an MgCl₂·6H₂O solution 690 showed a MDRH of 15.9 (\pm 0.3) %. The characteristic –OH vibration signatures from in-situ RMS 691 indicated the formation of MgCl₂·4H₂O, rather than thermodynamically stable MgCl₂·6H₂O, due 692 to a kinetic barrier to nucleation and structural growth with limited condensed water during the 693 dehydration process. The NaCl-MgCl₂ mixture particles with NaCl-rich compositions of $0.05 \leq$ $X_{\text{NaCl}} \leq 0.9$ mostly showed two-stage deliquescence: first, with the dissolution of eutonic 694 695 components, and second, with the complete dissolution of NaCl, typical for two component salt 696 systems (Gupta et al., 2015; Li et al., 2014). The second DRH values approach the pure NaCl limit 697 as the mole fraction of NaCl increases. Interestingly, NaCl-rich particles with composition of X_{NaCl} 698 = 0.1 and 0.2 showed three different mutual deliquescence behaviors during the humidification 699 process, which was also confirmed by complementary in-situ RMS measurements. The first type 700 showed an MDRH of 15.9 (± 0.3) %; the second type showed a first MDRH at ~ 15.9 (± 0.3) %, an 701 efflorescence-like transition to MgCl₂·6H₂O at RH in the range of ~ 16.1–24.9 %, and a second 702 MDRH at ~ 33.0 (± 0.5) %; and the third type showed an MDRH at ~ 33.0 (± 0.5) %. These phenomena are rarely observed for NaCl-rich particles of $0.3 \le X_{\text{NaCl}} \le 0.9$ and also $X_{\text{NaCl}} = 0.05$, 703

where most particles showed an MDRH at ~ 15.9 (± 0.3) %. Particles with MgCl₂-dominant compositions of $X_{\text{NaCl}} = 0.026$ (eutonic) and 0.01 mostly showed single-stage deliquescence behavior like pure MgCl₂·4H₂O particles with a DRH of 15.9 (± 0.3) %.

707 During dehydration, NaCl–MgCl₂ mixture particles of $0.05 \le X_{\text{NaCl}} \le 0.9$ showed two-stage 708 efflorescence: first, by the homogeneous nucleation of NaCl and second, by nucleation of the 709 eutonic component at MERH, which is mostly independent of the aerosol compositions. The first 710 ERH values approach the pure NaCl limit as the mole fraction of NaCl increases. MgCl₂-dominant 711 particles with the eutonic composition ($X_{NaCl} = 0.026$) and $X_{NaCl} = 0.01$ showed single-stage 712 efflorescence at ERHs ranging from 10.1 to 3.2 %. Most particles at all mixing ratios (0.01 $\leq X_{\text{NaCl}}$ \leq 0.9) showed MERHs in the range of 10.4–2.9 %, forming MgCl₂·4H₂O. On the other hand, a 713 714 significant number of particles with $X_{\text{NaCl}} = 0.1$ and 0.2 were observed to undergo a second 715 efflorescence at higher MERHs = 15.2-11.9 % and 23.7-15.3 %, respectively, to form 716 MgCl₂·6H₂O, which is coupled with the observation of the first MDRH at \sim 33.0 % during the 717 subsequent humidification process. The observation of MgCl₂·6H₂O efflorescence at relatively 718 higher RH ranges than MgCl₂·4H₂O efflorescence suggests that the presence of sufficient condensed water assists in hydrate-ion $[Mg(6H_2O)]^{2+}$ mobilization and that only optimally-sized 719 720 crystalline NaCl can act as heterogeneous nucleation seeds to overcome the kinetic barrier, leading 721 to the structural growth and crystallization of MgCl₂·6H₂O. SEM/EDX elemental X-ray mapping 722 showed that the effloresced NaCl–MgCl₂ particles of NaCl-rich mixing ratios had the NaCl moiety 723 homogeneously crystallized in the center, surrounded by MgCl₂·4H₂O, forming a core-shell 724 structure.

725 NaCl-MgCl₂ mixture aerosol particles can maintain an aqueous phase over a wider RH 726 range than the pure NaCl particles, both in the humidification and the dehydration modes, making 727 their heterogeneous chemistry with atmospheric gas phase species more likely. The hygroscopic 728 curves, Raman -OH vibrational signatures, phase diagrams obtained for DRHs and ERHs, and 729 chemical X-ray maps of effloresced particles covering twelve mixing ratios $(0.01 \le X_{\text{NaCl}} \le 0.9)$ 730 provided a clear picture of the hygroscopic behavior and chemical micro-structure of NaCl-MgCl₂ 731 mixture particles as nascent SSA surrogates. This can help characterize the mixing states, 732 morphology, phases, and aqueous phase chemistry of ambient, nascent inorganic SSAs.

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Table 1. Encountering frequencies (in %) of Types A, B, and C particles, showing different mutual deliquescence behavior (details in text), at various mixing ratios of NaCl–MgCl₂.

Mole fraction of	Encountering frequencies (in %)		
NaCl (X _{NaCl})	Type A particles	Type B particles	Type C particles
0.01	94	6	-
0.026	94	6	-
0.05	96	4	-
0.1	24	29	47
0.2	36	45	18
$0.3 \leq X_{NaCl} \leq 0.9$	100	-	-

Figure 1. Plot of 2-D area ratio (A/A_0) of nebulized pure (a) NaCl and (b) MgCl₂ as a function of the RH. The recorded transition RHs in both humidification and dehydration processes are marked with arrows.



Figure 2. Optical images and corresponding Raman spectra obtained by in-situ RMS, for a representative dry-deposited MgCl₂·6H₂O particle during (a) humidification (1st cycle), (b) dehydration (1st cycle), and (c) humidification (2nd cycle) processes and for a representative wet-deposited MgCl₂ particle during (d) humidification and (e) dehydration processes.



Figure 3. Plot of 2-D area ratio (A/A_0) of a NaCl-rich particle with a seawater-like mixing ratio of $X_{\text{NaCl}} = 0.9$ as a function of RH. The recorded optical images of the particle/droplet along with transition RHs in both humidification and dehydration processes are marked with arrows.



Figure 4. Plots of 2-D area ratio (A/A_0) of NaCl–MgCl₂ mixture aerosol particles with (a) NaCl-rich mixing ratio of $X_{NaCl} = 0.5$; (b) MgCl₂-dominant eutonic composition of $X_{NaCl} = 0.026$; and (c) MgCl₂-dominant mixing ratio of $X_{NaCl} = 0.01$ as a function of RH. The recorded transition relative humidification and dehydration processes are marked with arrows.



Figure 5. Plots of the 2-D area ratio (A/A_0) of three representative particles with a composition of $X_{NaCl} = 0.2$, showing different deliquescence behaviors during the humidification process, as a function of RH. During the humidification process, (a) "Type A" particle shows two deliquescence transitions with MDRH of 15.8 %, (b) "Type B" particle shows three deliquescence transitions as well as one efflorescence transition, and (c) "Type C" particle shows two deliquescence transitions with MDRH of 5.2 %, whereas the Type C particle shows a second ERH of 23.7 %. The recorded optical images of the particles/droplets along with the transition RHs during both humidification and dehydration processes are marked with arrows.



Figure 6. Characteristic OH-stretching Raman spectra and corresponding optical images of NaCl-MgCl₂ mixture particles with a composition of $X_{NaCl} = 0.2$, recorded by in-situ RMS. Three types of particles showing different hygroscopic behavior are shown. See the text for a detailed explanation.



Figure 7. Measured MDRHs (MDRH₁ = 15.9 (±0.3) % \Rightarrow open blue triangles; MDRH₂ = 33.0 (± 0.3) % \Rightarrow open brown circles) and the second DRH (closed black circles) and calculated MDRH (dotted red line) and the second DRHs (dash-dotted black curve) from the AIOMFAC, plotted as a function of the mole fraction of NaCl in NaCl-MgCl₂ mixture particles. The phase notations shown in brackets are: s = solid; and aq = aqueous. The brown shaded portion is where particles with three types of transitions (Types A, B, and C as in text) were observed for $X_{\text{NaCl}} = 0.1$ and 0.2. The dense and light brown shaded patterns indicate the high and low encountering frequencies of Types B and C particles, respectively. The average and range of ERHs observed during the humidification process for Type B particles are represented by purple stars and bars, respectively.



Figure 8. Measured first ERH values (closed black circles) and second ERH values (open blue triangles (MERH₁ for MgCl₂·4H₂O crystallization in Types A or B particles) and open purple stars (MERH₂ for MgCl₂·6H₂O crystallization in Type C particles)) as a function of the mole fraction of NaCl in NaCl-MgCl₂ mixture particles. The phase notations shown in brackets are s = solid; and aq = aqueous.



Figure 9. Elemental X-ray maps for Na (from NaCl), Mg (from MgCl₂), O (from MgCl₂·xH₂O), and mixed Na/Mg and secondary electron images (SEIs) of the effloresced NaCl-MgCl₂ mixture particles with compositions of (A) $X_{NaCl} = 0.9$ (NaCl-rich, seawater-like mixing ratio) and (B) $X_{NaCl} = 0.6$.

