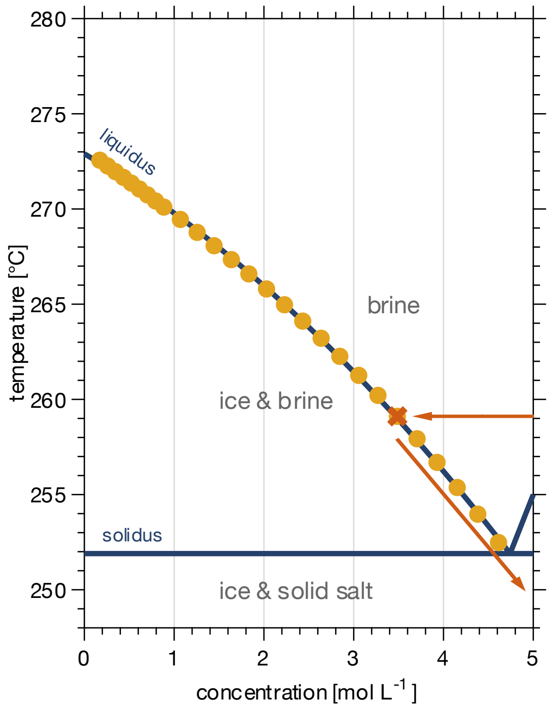
Bartels-Rausch et al. present an original piece of research, investigating the phase changes in the NaCl-water binary system by measuring NEXAFS spectra across the chlorine K-edge when varying the temperature- and relative humidity conditions the particles are exposed to. The assignment of the three basic spectra types recorded for anhydrous NaCl particles, aqueous NaCl solution droplets, and the first-time mea- surement for hydrohalite, are convincing. I do not have any major concerns regarding the scientific content and quality of the manuscript, but I would strongly encourage the authors to improve to some extent the way of presentation of the data, and thereby better "guide the reader" through the various parts of the article.

We thank the referee for the supporting judgement of the manuscript.

Major comment:

All the while reading the section "NEXAFS of brine, halite, and hydrohalite", I kept won- dering how exactly the experiment was carried out, i.e., what was the actual trajectory in the T-RH space, how exactly was the freezing of the NaCl solution droplets induced, how did you move along the ice/NaCl(aq) equilibrium line, how was hydrohalite with- out ice (Fig. 3F) formed? All these experimental details are only provided in later parts of the article (e.g. line 348ff, line 442ff). I see some good reason for the chosen manuscript structure, i.e., that you first want to describe the NEXAFS spectra, discuss some technical aspects like spectra quality and reproducibility, compare your measure- ments with literature spectra - and then later discuss the exact formation conditions for hydrohalite and the atmospheric implications based on the T-RH trajectory. But having a better general idea of the experimental procedure before reading the section with the NEXAFS spectra would be in my opinion a clear improvement regarding the clarity of presentation. One suggestion would be the following: On line 84, you introduce the NaCl-water phase diagram, but describe it with some "hypothetical" trajectory, starting from a sample below 251.9 K and then increasing the temperature. But why not discuss the phase diagram with a "proper" trajectory from your experiments, which could be schematically depicted in Fig. 2 – meaning you start with an aqueous NaCl solution droplet, induce some supercooling to nucleate ice, and then move along the liquidus curve towards the eutectic and below, to investigate at which point hydrohalite precipitates. This is also the trajectory during which most of the spectra shown in Fig. 3 (B – E) were recorded (apart from the anhydrous NaCl, A, and the "ice-free" hydrohalite, F. At the end of the introduction or at the beginning of the "NEXAFS of brine, halite, and hydrohalite" section, you should then include a paragraph and inform the reader about the general structure of the manuscript, i.e., that you want to disentangle the detailed description of the NEXAFS spectra of the three species (shown first) from the detailed analysis of the phase changes when moving in the T-RH space (shown later). Please also number all section and subsection headings correctly.

This is a splendid idea that we will happily follow. Thank you. Figure 1 and the paragraph describing it will be updated as follows:



«Figure 2: Phase diagram of the NaCl-water binary system. The data show the freezing point depression of sodium-chloride solutions (yellow filled circles) and give the concentration of an aqueous sodium chloride solution in equilibrium with ice in the temperature range of 273 K to 254 K (Rumble). The dark blue lines indicate the phase boundaries (Koop et al., 2000b; Rumble), that is it denotes the so-called liquidus and solidus line, respectively, and thus shows the temperature and concentration range where ice and aqueous sodium chloride solution co-exist. The eutectic temperature of sodium chloride – water binaries is 251.9 K (Koop et al., 2000a). Also shown is a typical experimental procedure (red arrows and cross).»

"While the phase diagram of sodium chloride – water binary mixtures and the thermodynamic stability domains of salt, solution, and ice are well known (Koop et al., 2000a), the precise occurrence of nucleation and sodium chloride precipitation is still debated (Koop et al., 2000a; Wise et al., 2012; Peckhaus et al., 2016). Figure 2 shows a part of phase diagram of sodium chloride - water mixtures and can be used to illustrate the appearance of the individual phases. Below 251.9 K, the eutectic temperature of sodium chloride (Koop et al., 2000a), solid sodium chloride dihydrate (hydrohalite, NaCl•2H2O) and solid water (ice) are the energetically favoured phases. Between the eutectic temperature and the so-called liquidus line, ice and sodium chloride solution (brine) co-exist. The ice will melt completely above the liquidus line, and an aqueous sodium chloride solution is the only phase present. The focus of this work was to experimentally observe phase changes of sodium chloride below the eutectic temperature. A typical experimental procedure started with a dry sample of anhydrous sodium chloride (halite, NaCl) which was exposed to increasing gas-phase water at constant temperature of 259 K. By absorbing water from the surrounding air, a phase transition from the solid salt to a liquid solution (deliquescence) took place. Upon increasing the gas-phase water dosing further (Fig. 2, red arrow) ice crystalised and a two-phase system of ice and brine occurred (Fig. 2, red cross). After probing the sample at this

position in the phase diagram (see below), temperature was lowered and the dosing of the water-vapor adopted to move along the liquidus line to below the eutectic temperature to perform additional measurements. During this cooling period, salt concentration and volume of the brine changes. Such changes with varying relative humidity (hygroscopic growth) have long been discussed for aerosol in the troposphere. In other words,…"

Additional comments:

1) Regarding line 88 and 112: Isn't 251.9 K the ice-hydrohalite eutectic, and shouldn't ice and NaCl*2H2O be the energetically favored phases below that temperature?

Yes, you are correct. Apologies for the confusion. In this early part of the manuscript, we tried to mention "sodium chloride" in the sense of a salt of sodium chloride (halite or hydrohalite). We will be careful to me more specific in the revised version.

Line 88: «Oldridge and Abbatt (2011) showed that the rate of the heterogeneous reaction of ozone with bromide in sodium chloride -- water mixtures is strongly reduced once the salt precipitates below 252 K.»

Line 112: «Below 251.9 K, the eutectic temperature of sodium chloride (Koop et al., 2000a), solid sodium chloride dihydrate (hydrohalite, NaCl•2H2O) and solid water (ice) are the energetically favoured phases.»

2) Line 279/280: "249 K in the presence of ice and at 244 K in the absence of ice": When reading this sentence for the first time, I was also wondering whether spectra 3E and 3F were from the same trajectory and asked myself how the experimental procedure could have been – it is only explained much later (line 441ff). You should include here at least a short description of how the particles from spectrum F were generated.

Thanks, done. We have added a sentence stating the relevance of spectra in Figure 3C-E and separated the discussion of the spectra in Fig. E and F:

Line 245: "Figure 3C-E show NEXAFS spectra acquired in the ice stability domain at temperatures below the eutectic temperature of 251.9 K (Koop et al., 2000a). By comparing these spectra to the spectra in Fig. 3 A-B, the phase of the sodium chloride in presence of ice below the eutectic temperature will be discussed."

Line 279: "Figure 3E shows a spectrum after warming the sample back to 249 K in the presence of ice. Clearly, the observed shape in region I show that hydrohalite and not liquid brine is the dominant phase of this sample. In Fig. 3 F a spectrum at 244 K in absence of ice is shown, again the shape is in good agreement to spectrum shown in Figure 3D."

3) Line 337: Here starts the detailed discussion of the phase behavior of the particles in the T-RH space. I would also appreciate an introductory paragraph describing how this section is structured and what different aspects are discussed. Otherwise, the reader may quickly lose track of things. For example, the heading "Liquid below eutectic and nucleation" in line 347 comprises a very long section that could be divided into various subsections. In the headings, you could also be more specific what you mean by "nucleation", nucleation of ice or the precipitation of hydrohalite.

Thanks, done.

«Now that we have identified halite, the hydrohalites, and the aqueous solution by means of the NEXAFS spectra at the interfacial region, we discuss their observation in the phase diagram. Generally, we have observed solid sodium chloride as halite or hydrohalite at temperatures below 240 K and at 44 % to 79 % RH and brine in the temperature range of 248 K to 259 K and RH of 78 % - 88 %.
Interestingly, the NEXAF spectra have revealed the dominant presence of brine in one sample and of hydroahliate in other samples. All these samples were probed below the eutectic temperature indicating that not only the temperature and relative humidity, but also the trajectory to reach these settings (or the history of the sample) might determine the phase. Therefore, we will detail the humidity and temperature history of each sample in the following in detail. Also, we will compare our findings to the extensive literature work of observed phases in presence and absence of ice. This discussion will be based on the sodium chloride – water phase diagram in the temperature – relative humidity space (Figure 4A) as initially constructed by Koop et al. (2000a).»

4) Line 353: Can you please quantify "modest" supersaturation – did you need to reach the homogeneous freezing limit for aqueous solution droplets (Koop et al., 2000b) or did the surface catalyze heterogeneous ice nucleation?

Thanks, for mentioning homogeneous freezing. We will certainly add this detail to a revised version. The homogeneous freezing temperatures reported by Koop at 60-90% RH are about 210-230K, lower than the temperature range of this study.

"Then, the relative humidity was further increased to cross the ice stability line until ice nucleation occurred at a modest oversaturation of typically 90 % to 95 % relative humidity at 259 K. Ice nucleation was evident by a sharp pressure drop from the pressure dosed to the cell to the water vapor pressure of ice at that temperature, for example 88 % relative humidity at 259 K. In some experiments, temperature was lowered 1 K to 2 K as well to trigger ice nucleation. Please note, that temperature was always well above the homogenous freezing temperature, which was found at 210 K to 230 K at relative humidities of 60 % to 90 % {Koop, 2002}. "

5) Line 442, regarding the trajectory when recording spectrum 3F: Could you please elaborate a bit more on the idea and temporal order behind this trajectory (Fig. 4C), I did not quite understand how the procedure was – did you again try to cool a NaCl droplet along the liquidus curve but without inducing sufficient supersaturation to nucle- ate ice? And then at about 244 K reduced the RH to 59% to induce the crystallization of hydrohalite? And then increased RH back to 73%

Apologies for being not clear. The reasoning behind this experiment was to observe hydrohalite in absence of ice. In this set, we started with brine in absence of ice by evaporating the water (decreasing RH to ~70%) at 252K. then we lowered the temperature to 247K at constant partial pressure of water (so the RH increases to > 80%). We crossed the ice stability line, but supersaturation was not sufficient to nucleate ice. We repeated this procedure to reach the RH-T positions "F".
We will elaborate this procedure in more detail in the revised manuscript.

Hydrohalite can also precipitate in absence of ice by evaporating water from a solution at temperatures below 273 K (Craig et al., 1975; Yang et al., 2017). Such a trajectory, that is the temperature and water vapor pressure the sample experienced, is shown in Fig. 4C (green solid line). In this set of experiments, from a brine sample in absence of ice at 252 K (above the eutectic temperature) water was evaporated by decreasing the relative humidity to about 70 % at 252 K, followed by lowering the temperature to 247 K at constant partial pressure of water (so that the relative humidty increased to about 80 %). When the ice stability line in the phase diagram was crossed, ice nucleation was not observed as the oversaturation was not sufficient to trigger ice nucleation. This procedure was repeated to further lower the temperature to 244 K at 59 % relative humidity. Then, the first NEXAFS was recoreded at 244 K and 59 % RH (Fig. 4, green diamond), where in absence of ice nucleation was visually observed. The location in the phase diagram is in agreement with Wagner et al. (2012)'s observation of salt deposits in aerosol droplets in an aerosol chamber (AIDA)in absence of ice. The second NEXAFS spectra resembling that of the hydrohalite and in absence of ice was recorded at a slightly higher relative humidity of 72 % (Fig. 4, green diamond). Both NEXAFS spectra (Fig. 4, green diamonds) were identified as hydrohalite (Fig. 3F). The sample at 44 % RH (Fig. 4C, blue line) has been exposed to 0 % RH prior to acquiring the NEXAFS spectrum (Fig. 4, blue square), which removes the crystal water (Light et al., 2009; Wise et al., 2012).

technical corrections:

Thanks, all technical correction are done.

1) Doesn't the title sound a bit awkward? Maybe better: "Investigation of interfacial supercooling . . ." or ". . . NaCl solutions studied by X-ray absorption spectroscopy"
2) Line 86: "shows a part of the phase diagram"
3) Line 109: "in equilibrium with ice"
4) Line 115 – 117: Very long sentence, please split into two.
5) Line 138: "nitrate and chloride form solvation cells"
6) Line 173: "and with a pass energy"
7) Line 186: "take-off angle of detected electrons (?)"
8) Line 220: photon energy in eV
9) Line 240: Br- (superscript is missing)
10) Line 338: "the hydrohalite"
11) Line 353: maybe better "supersaturation"
12) Line 355: maybe: "and is thus a sole function"
13) Line 411/412: This is a pretty nested sentence, please re-phrase.
14) Line 416: "in larger patches/inclusions"
15) Line 444/445: The sentence seems incomplete, it also misses the point at the end.
16) Line 450: Fig. 3A
17) Line 462: check super- and subscripts