

***Interactive comment on “Novel method of generation of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{CaCO}_3$  aerosols and first determination of hygroscopic and cloud condensation nuclei activation properties” by D. F. Zhao et al.***

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We would like to thank the reviewer for the comments and suggestions, which contribute to improve the quality of our paper. We have made revisions and have answered to all the comments and suggestions. Please, find a detailed response to each comment below.

General Comments

Zhou et al. describe the characterization of calcium mineral particles generated using

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a new method. This involves atomizing a saturated solution of calcium bicarbonate and annealing the particles in a tube furnace to convert  $\text{Ca}(\text{HCO}_3)_2$  to  $\text{CaCO}_3$ , presumably producing calcite. As the generation of suspended mineral particles with the appropriate physical and chemical properties is challenging, and they represent an important source of atmospheric particulate matter, this paper will be of interest to the Atmospheric Chemistry & Physics readership. I have several major concerns and suggestions regarding this manuscript. This paper presents several interesting findings from the characterization of particles using this new generation method. However, the manner in which the paper is organized and written creates difficulties in understanding these findings and their interpretation. I recommend that Major Revisions be made to address these issues before the paper can be re-considered for publication in ACP.

Response: We thank the reviewer for making us aware that parts of the manuscript are not as clearly written as we thought. The purpose of the paper was to demonstrate a new method to generate water-insoluble  $\text{CaCO}_3$  particles in controlled manner by spraying bicarbonate solutions, drying, and annealing the aerosol afterwards. The focus should supposedly have been on characterization of composition and properties of these particles by AMS, CCN and HG measurements. In addition, we studied some aspects of long term change of HG and CCN properties in our large aerosol chamber for dry air and ambient air and in presence of  $\text{NO}_x/\text{HNO}_3$ . From this point of view, the principal organization of the paper seems still to be suited and we would prefer not to change the overall structure. However, we added new paragraphs and modified paragraphs according to the general and specific comments. We tried to come up to all the requests of the reviewer, which were within the scope of our manuscript.

Summary of major changes:

A) We understood that a few of our notations were confusing and we changed it. In the laboratory study:

- the aerosols were always dried to <5% before any analysis. This is now more often ex-

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plicitly stated. In the old manuscript we silently assumed that the dried particles before annealing were solid and omitted to characterize their physical state explicitly as solid. In the revised manuscript, we now summarized our evidence that these particles were solid  $\text{Ca}(\text{HCO}_3)_2$  and formulated as a hypothesis that we may have observed solid  $\text{Ca}(\text{HCO}_3)_2(\text{s})$ . Once the hypothesis was formulated we characterized  $\text{Ca}(\text{HCO}_3)_2$  particles as solid throughout the manuscript with the qualifier (s).

- in the hygroscopicity section 3.4: we pre-conditioned particles in one experiment by bringing them to 100% RH and drying them again. We called these wet-processed  $\text{Ca}(\text{HCO}_3)_2$  in the old manuscript. Since we know the composition of these particles, we call them now mixed  $\text{Ca}(\text{HCO}_3)_2/\text{CaCO}_3(\text{s})$  particles, in contrast to the unprocessed particles  $\text{Ca}(\text{HCO}_3)_2(\text{s})$ . As shown by HG measurements also the mixed particles were solid and will be qualified by (s). We also omitted the notations wet-conditioned, wet-processed etc. and replaced it by pre-conditioned, since the particles were always dried.

- we showed that on the time scale of one hour which is needed to measure humidograms  $\text{Ca}(\text{HCO}_3)_2(\text{s})$  particles are partially converted into mixed  $\text{Ca}(\text{HCO}_3)_2/\text{CaCO}_3(\text{s})$  particles. In the CCN measurement we don't know how much of the  $\text{Ca}(\text{HCO}_3)_2(\text{s})$  is converted into mixed particles during the  $\sim 15$  s of residence time. In the CCN section we classified the particles according to their state before entering the CCN counter as  $\text{Ca}(\text{HCO}_3)_2(\text{s})$ , mixed  $\text{Ca}(\text{HCO}_3)_2/\text{CaCO}_3(\text{s})$ , or  $\text{CaCO}_3$ .

These notations were also used for long term chamber studies in the revised manuscript.

B) We extended the quantitative analysis of our HG and CCN measurements by applying one parameter Köhler equation ( $\kappa$ ). We also summarized proof from this analysis that the  $\text{Ca}(\text{HCO}_3)_2(\text{s})$  and  $\text{Ca}(\text{HCO}_3)_2/\text{CaCO}_3(\text{s})$  particles were indeed solid. The  $\kappa$  serve now also to compare with the chamber results and literature data.

C) We changed the conclusions expressing more clearly our evidence for

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$\text{Ca}(\text{HCO}_3)_2(\text{s})$ , but we will remain on level of hypothesis since we don't have the experimental tools to prove the physical state beyond doubt.

As the purpose of the paper was to present a new method to generate  $\text{CaCO}_3$  (and possibly  $\text{Ca}(\text{HCO}_3)_2(\text{s})$ ) particles as well as their characterization with respect to composition and hygroscopicity on different time scales and humidity regimes, we object to extent our manuscript with respect to considerations of thermodynamics of  $\text{Ca}(\text{HCO}_3)_2(\text{s})$ , detailed mechanism of its formation or its heterogeneous conversion. All these suggestions by the reviewer were well taken, however we don't have the proper data and tools for doing so and these suggestions are going far beyond the scope of this single manuscript.

We added new Table 4 and 5 giving the critical parameters of CCN activation from the laboratory study and an overview over the Large Chamber experiments, respectively. We also removed some minor errors in the manuscript, especially in the hygroscopic growth section 3.4 the RHs for onset of restructuring were 2-3% off in the text and in Figure 8. The numbers given in Fig. 8 were correct and this has been changed in the text accordingly.

In order to reply to the further general comments we broke it down in smaller parts which we numbered. If not stated otherwise the page and line numbers refer to the revised version of the manuscript. All changes are highlighted in the revised version of the manuscript.

General Comments (part 1): The major issue regards calcium bicarbonate itself. This compound is not thought to exist in a stable solid form of any kind, existing only as its dissociated ions in an aqueous solution. However, Zhou et al. appear to present evidence for both the generation of solid  $\text{Ca}(\text{HCO}_3)_2$  particles, and the stability of these particles while suspended in dry air over the period of hours. First, the novelty of these findings should be made clear in the manuscript, by referring to the calcium bicarbonate particles as solid when the experimental evidence supports this conclusion. More

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importantly, some discussion of this unexpected behavior is required; none exists in the current manuscript. It would be a great help if the physical phase of the various compounds were noted as "(s)", "(aq)", etc. when there is evidence or good reason to support this.

Response (part 1): The reviewer raised two important questions: the physical phase state of the "long lived  $\text{Ca}(\text{HCO}_3)_2$ " aerosol and the organization of the discussion of this finding.

We modified and extended the discussion of the state of  $\text{Ca}(\text{HCO}_3)_2$  in the revised manuscript.

But first we would like to emphasize that the main focus of the manuscript was not the possible observation of a new metastable, solid, phase of  $\text{Ca}(\text{HCO}_3)_2$ . We described the generation of solid  $\text{CaCO}_3$  particles and their chemical and microphysical characterization (the latter as diagnosis tool) - in comparison to the precursor aerosol before annealing. It took us by surprise that this precursor aerosol appeared to be pure  $\text{Ca}(\text{HCO}_3)_2$  within the errors of Q-AMS analysis. There is a good chance that this aerosol is a solid, but we can only conclude this indirectly from slow growth and the restructuring observed in the HG measurements. If there was solid  $\text{Ca}(\text{HCO}_3)_2$ , this interesting phenomenon would be worth more intensive studies. But these are clearly beyond the scope of the presented manuscript. Nevertheless, it was important to hypothesize that solid  $\text{Ca}(\text{HCO}_3)_2$  may exist and to point this out to the community, as we obviously have observations compatible with such a hypothesis.

Having stated that, back to state of matter of the  $\text{Ca}(\text{HCO}_3)_2$  aerosol. From all our measurements we cannot tell for sure, if the particles are solid or not: we dried the fresh aerosol generated by spraying the  $\text{Ca}(\text{HCO}_3)_2$  solution with a diffusion drier to  $\text{RH} < 5\%$  in the lab-scale study. The final  $\text{RH} < 5\%$  in the drying tube was not given in the manuscript, but is now added in the revised manuscript. In a similar way, we dried the freshly sprayed aerosol by spraying it into the Large Aerosol Chamber pre-conditioned

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to  $< 3\% \text{RH}$  and featuring  $5\% \text{RH}$  after introducing the aerosols. This procedure was described in the old manuscript in section 2.6. We will now use in the first parts of the revised manuscript the qualifier "dried" in context with the sprayed aerosols from  $\text{Ca}(\text{HCO}_3)_2$  solutions, which were always dried before further investigation. This will not tell if the particles are solid or liquid, but will clarify at least that we do not refer to droplets of dilute  $\text{Ca}(\text{HCO}_3)_2$  solutions.

The Q-AMS analysis of the dried aerosols and the afterwards annealed aerosols showed

- no excess water
- stoichiometric  $\text{H}_2\text{O}/\text{CO}_2$  ratios as expected for  $\text{Ca}(\text{HCO}_3)_2$

We stated now more clearly that we have observed pure  $\text{Ca}(\text{HCO}_3)_2$  before and pure  $\text{CaCO}_3$  after annealing in the tube furnace - within the errors limits of the Q-AMS measurement.

We added the information that the aerosol were dried before AMS measurement to the last sentence regarding the Q-AMS analysis (p. 13, line 19)

"All other evidence supported that we produced pure  $\text{Ca}(\text{HCO}_3)_2$  aerosol by spraying the solution and drying the aerosol to  $\text{RH} < 5\%$  and that we were able to convert it to  $\text{CaCO}_3$  by annealing it to  $300^\circ \text{C}$ ."

At the end of the computational analysis of the particle composition (p. 14, line 21.), we modified in the revised manuscript:

"Based on the analysis of the composition of the aerosol above, we will refer to the dried aerosol before annealing in the furnace as  $\text{Ca}(\text{HCO}_3)_2$  aerosol and to the aerosol after annealing as  $\text{CaCO}_3$  aerosol in the following."

And we added the sentences on (p. 14, line 23):

"We hypothesize that the  $\text{Ca}(\text{HCO}_3)_2$  particles were solid, although it is known that

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solid  $\text{Ca}(\text{HCO}_3)_2$  is thermodynamically instable at ambient conditions. The  $\text{CaCO}_3$  particles were pure solids within the errors of the analysis but may have contained traces of  $\text{Ca}(\text{HCO}_3)_2$ .

Regarding the qualifiers (s), (aq) etc. proposed by the referee, there was no need to qualify the physical state of the aerosols up to this point of the manuscript. From here on we follow the suggestion of the reviewer and qualify the state of the aerosols by (s) etc. where reasonable. We would like to mention that in all chemical equations R1-R4 these qualifiers were already given in the original manuscript.

General Comments (part 2): What processes might allow  $\text{Ca}(\text{HCO}_3)_2$  to form stable solid particles when this compound is not known to exist in a solid form? Note that in (R1) the product is  $\text{Ca}(\text{HCO}_3)_2(\text{aq})$ , not a solid. How do the authors propose that solid  $\text{Ca}(\text{HCO}_3)_2(\text{s})$  forms? Has it ever been observed to precipitate from  $\text{Ca}(\text{HCO}_3)_2$  solutions, with or without heat/annealing? Are there any previous reports of solid  $\text{Ca}(\text{HCO}_3)_2$  being generated under similar or dissimilar environmental conditions?

Response (part 2): We simply do not know more than that the water obviously evaporated. We have no tools to further investigate those interesting questions.  $\text{Ca}(\text{HCO}_3)_2(\text{s})$  must be metastable. Whenever a thermodynamic metastable modification is formed, a kinetic hindrance must be involved. In our case fast/sudden evaporation of water seems to limit the formation of  $\text{CaCO}_3$ . But this is pure speculation. We added the following in the revised manuscript (p. 16, line 3):

"The moderate growth at  $\text{RH} < 71\%$  of the non-processed, dried  $\text{Ca}(\text{HCO}_3)_2$  particles and the restructuring supports our hypothesis that these particles were solid. It must be a metastable solid phase; the sudden evaporation of water in the drying process seems to hinder the formation of thermodynamically stable  $\text{CaCO}_3$ . Also the preprocessed, mixed particles did not show growth at  $\text{RH} < 92\%$  although they contained 33%  $\text{Ca}(\text{HCO}_3)_2$ . This indicates that these mixed particles were also solid."

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Reaction R1 describes the weathering reaction, we took advantage of it to generate the  $\text{Ca}(\text{HCO}_3)_2$  solutions. It also predicts that we should expect the formation of  $\text{CaCO}_3$  if during the drying process also  $\text{CO}_2$  is evaporating. This is obviously not the case, if one spray-dries the  $\text{Ca}(\text{HCO}_3)_2(\text{aq})$  aerosols. However, there was an error on p. 8021, line 19 and p. 8028, line 7 in the old manuscript, here it should read Reaction R2 (instead of Reaction R1). We apologize for this misleading error and corrected it in the revised manuscript.

To our knowledge there were no other reports on formation, precipitation, annealing of solid  $\text{Ca}(\text{HCO}_3)_2$  under similar or dissimilar environmental conditions than those quoted, when we submitted the manuscript. Calcium bicarbonate may precipitate from solutions if  $\text{CO}_2$  pressures  $> 50$  bars are applied or at low temperatures (Keiser and Leavitt, 1908). A review of literature until 1960 can be found in Gmelins Handbuch der anorganischen Chemie 8th, Calcium, Teil B- Lieferung 3, System-Nummer 28, p.927-943.

General Comments (part 3) The paper should be re-organized so that the evidence supporting the formation of solid calcium bicarbonate is more clear. From my reading this evidence seems to include: (1) the observed humidogram in which supposed  $\text{Ca}(\text{HCO}_3)_2$  particles shrink  $> 80\%$  RH but do not begin to grow until  $\text{RH} > 92\%$ , (2) TEM images of the particles before and after annealing, and (3) the difference in observed nitrate formation in the particles under dry versus humid chamber experiments.

Response (part 3): We added the according paragraphs in the concluding section (p.22, line 2):

In this study, a novel, easy to operate method was developed using atomization of a  $\text{Ca}(\text{HCO}_3)_2$  solution to produce  $\text{CaCO}_3$  aerosol, one of the most reactive components in mineral aerosol. In this procedure  $\text{CO}_2$  was bubbled through a slurry of  $\text{CaCO}_3$  dissolving it as bicarbonate. The supernatant solution was decanted, sprayed with an atomizer and dried. Annealing the aerosol in a tube furnace at  $300\text{ }^\circ\text{C}$  promoted the

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conversion back to CaCO<sub>3</sub>.

Q-AMS measurements confirmed that the particles after annealing consisted of pure CaCO<sub>3</sub>. By hygroscopic growth measurements we derived a hygroscopicity parameter  $\kappa$ (97%RH) of  $0.0016 \pm 0.0004$  for the CaCO<sub>3</sub> particles, which agreed with the  $\kappa$  of  $0.0019 \pm 0.0007$  obtained by measurements of CCN activation. The  $\kappa$  from both methods agree very well within the errors and with the  $\kappa$  of  $0.0011 \pm 0.0004$  reported by Sullivan et al. (2009b) for dry-dispersed CaCO<sub>3</sub> powder. The new method is suited to generate CaCO<sub>3</sub> aerosol of sufficiently high concentration and proper size for studies of hygroscopicity, CCN activity and aerosol chemistry studies in simulation chambers.

Q-AMS measurements further confirmed that the particles obtained by spraying Ca(HCO<sub>3</sub>)<sub>2</sub> solutions and drying the aerosol to RH<5% consisted of pure Ca(HCO<sub>3</sub>)<sub>2</sub>. This finding could be highly interesting as we have indication that these particles were solid, although Ca(HCO<sub>3</sub>)<sub>2</sub>(s) is thermodynamically unstable under ambient conditions. TEM showed that the Ca(HCO<sub>3</sub>)<sub>2</sub> particles were solid and spherical like the CaCO<sub>3</sub> particles, with Ca(HCO<sub>3</sub>)<sub>2</sub>(s) particles having some internal structures, bubbles or hollow pits. Since in the Q-AMS study pure Ca(HCO<sub>3</sub>)<sub>2</sub> was observed without excess water, we can rule out inclusions of Ca(HCO<sub>3</sub>)<sub>2</sub> solution or the formation of metastable hydrates. In addition, Ca(HCO<sub>3</sub>)<sub>2</sub>(s) featured restructuring at 71% RH, which should not be observed in case of liquid particles. Processing the Ca(HCO<sub>3</sub>)<sub>2</sub>(s) particles at 100% RH and drying it again to <5%RH produced mixed CaCO<sub>3</sub>/Ca(HCO<sub>3</sub>)<sub>2</sub>(s) particles. These mixed particles must have been solid too, since they did not show noticeable hygroscopic growth below 92%RH and GF at 95% was only 1.03. The mixed particles and pure Ca(HCO<sub>3</sub>)<sub>2</sub>(s) were much better CCN ( $\kappa \approx 0.15 \pm 0.02$ ) than pure CaCO<sub>3</sub> ( $\kappa \approx 0.0019 \pm 0.07$ ). The difference in CCN activation and hygroscopic growth can be deduced to the limited solubility of Ca(HCO<sub>3</sub>)<sub>2</sub>(s) and a deliquescence point of larger than 97.5%RH, that was not assessable by our HTDMA. We therefore hypothesize that we have observed a new, solid phase of Ca(HCO<sub>3</sub>)<sub>2</sub>(s). This must have been a metastable phase and the formation of CaCO<sub>3</sub> according reac-

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tion R1 may be hindered when water of the solution evaporates rapidly in the diffusion dryer.

In the dry Large Aerosol Chamber Ca(HCO<sub>3</sub>)<sub>2</sub>(s) was converted over hours to a mixed salt containing  $\approx 40\%$  Ca(HCO<sub>3</sub>)<sub>2</sub>(s) and  $\approx 60\%$  CaCO<sub>3</sub>. The uptake of HNO<sub>3</sub> was slow probably due to a kinetic hindrance observed before on solid CaCO<sub>3</sub> particles (Vlasenko et al. 2009). In the dry chamber Ca(HCO<sub>3</sub>)<sub>2</sub>(s) could probably only persist, because it was protected by a CaCO<sub>3</sub> coating. Ca(HCO<sub>3</sub>)<sub>2</sub>(s) was shorter lived at 40% RH in ambient Jülich air in the presence of HNO<sub>3</sub> ( $\approx 1$  ppb) as well as in synthetic air in presence of several hundred ppb NO<sub>x</sub> and O<sub>3</sub>. In the latter case, carbonate contributed still about  $\sim 36\%$  (including 6% bicarbonate) after about one day and nitrate accounted for  $\sim 64\%$  (molar content) of the total calcium salt.

General Comments (part 4) Along with this it is important to specify what physical phase the authors believe the particles to exist in during the various experiments, particularly when the hygroscopic growth and CCN activation data are interpreted. Currently it is completely unclear to me how the authors interpret the humidograms and CCN activation results for the various particle systems. A thermodynamic explanation that reconciles the two types of water uptake experiments must be presented.

The HTDMA humidograms present evidence that the Ca(HCO<sub>3</sub>)<sub>2</sub> particles were solid after drying and before annealing. Otherwise aqueous particles would have exhibited continuous hygroscopic growth. Instead these particles appeared to have shrunk due to structural rearrangement, and only grew above a high RH of 92%. The implications of these observations and how they support the hypothesis of solid Ca(HCO<sub>3</sub>)<sub>2</sub> should be made clear in the manuscript. An interpretation of why the particles do not begin to grow until > 92% RH is also required. This RH value is higher than that of typical soluble inorganic salt systems, yet below that for insoluble compounds such as CaCO<sub>3</sub>(s). Can the properties of Ca(HCO<sub>3</sub>)<sub>2</sub>(s) explain this, or does it indicate contamination by more soluble hygroscopic compounds?

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Response: The referee raised the important point of interpretation of our humidograms and CCN measurements. Indeed, we were able to present the composition (not the physical state) of all aerosol types before they entered the analytical instruments, even of the pre-conditioned aerosol with 67% carbonate 33% bicarbonate. We also proposed a way how the mixed salt may have formed. We were not able to determine composition and state of the aerosols during the humidification process. However the non-processed and pre-processed aerosols exhibit the same behavior at high RH and thus possibly have similar composition. This was stated in the old manuscript (p. 8025, l. 5):

"When the growth curve of the non-conditioned aerosol was shifted using the diameter of the minimum at RH 89.5 % as reference diameter (Fig. 8, middle blue), the high humidity branches at RH > 93 % for the particles with and without wet-conditioning agree within the errors, thus should have the same composition and morphology."

And further (p. 8025, l. 13):

"In comparison to the pure CaCO<sub>3</sub>, the presence of Ca(HCO<sub>3</sub>)<sub>2</sub> increased the growth factors and thus shifted the growth curve to lower RH."

We cannot explain the observed behavior of the mixed salt e.g. by mixing rules since neither the composition as f(RH) nor Ca(HCO<sub>3</sub>)<sub>2</sub>(s) and its properties are known. Within the purpose and scope of this manuscript we don't see the need to extend this aspect.

The solubility of Ca(HCO<sub>3</sub>)<sub>2</sub> can be deduced from observations in the older literature.

We added this to section 3.4 in the revised manuscript (p. 18, line 9):

"Both,  $\kappa_{CCNpc} = 0.16$  and  $\kappa_{CCNnc} = 0.14$  are much larger than the corresponding  $\kappa_{GFpc}$  and  $\kappa_{GFnc}$  of 0.011 and 0.08. This can be explained by the limited solubility of Ca(HCO<sub>3</sub>)<sub>2</sub> described in the literature. The solubility of CaCO<sub>3</sub> is  $\approx 0.015 \text{ g/l} = 1.5 \cdot 10^{-4} \text{ mol/l}$  in a CO<sub>2</sub> free atmosphere at 25° (Gmelin 1961, p. 933). Raising

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the CO<sub>2</sub> pressure up to 1 bar (e.g. by bubbling CO<sub>2</sub> to CaCO<sub>3</sub> slurry) increases the solubility by a factor of 50 to about 0.008 mol/l (Gmelin 1961, p. 933). The additionally dissolved CaCO<sub>3</sub> with increasing CO<sub>2</sub> pressure exists as HCO<sub>3</sub><sup>-</sup> in the solutions (Gmelin 1961, p.927). We approximate the saturation concentration of Ca(HCO<sub>3</sub>)<sub>2</sub> by about 0.01 mol/l at room temperature and the according saturation mole fraction by  $0.01/(0.01+55.5) \approx 0.0002$ . The corresponding saturation ratio for an ideal solution would be 0.9998. We thus estimate a deliquescence humidity of Ca(HCO<sub>3</sub>)<sub>2</sub> around 99% RH. This estimate is reconcilable with our observations of minimal hygroscopic growth for the mixed salt below 92%RH and the absence of deliquescence below 97.5%RH (Fig.8, green squares). Ca(HCO<sub>3</sub>)<sub>2</sub> appears to be a non-hygroscopic salt below 97.5%RH because of its high deliquescence point, but a good CCN because of its still notable solubility."

(Onset of hygroscopic growth before the nominal deliquescence point has been observed for solids with low lattice energy (e.g. organic acids). As bicarbonate is thermodynamically unstable one can presume that the lattice energy here is also small. (Actually, one could speculate that the instability of Ca(HCO<sub>3</sub>)<sub>2</sub> may be attributed to the entropic effect of releasing gaseous water and CO<sub>2</sub> when converting to carbonate. This could mean that the formation of bicarbonate may be slightly exotherm, while overall endergonic. But these are speculations that were not considered in the revised manuscript.)

General comments (part 5) For example, in the Abstract you state, "Fresh Ca(HCO<sub>3</sub>)<sub>2</sub> particles are somewhat more hygroscopic than CaCO<sub>3</sub> particles although both have small growth factors of 1.03 and 1.01, respectively, at 95% relative humidity. The CCN activity of Ca(HCO<sub>3</sub>)<sub>2</sub> aerosol is remarkably higher than that of CaCO<sub>3</sub> aerosol and only slightly less than that of Ca(NO<sub>3</sub>)<sub>2</sub>." Why is Ca(HCO<sub>3</sub>)<sub>2</sub> nearly as hygroscopic as Ca(NO<sub>3</sub>)<sub>2</sub> above water saturation but nearly non-hygroscopic at 95% RH? Ca(NO<sub>3</sub>)<sub>2</sub> should exhibit a much larger GF than 1.03 at 95% RH. This could be explained by Ca(HCO<sub>3</sub>)<sub>2</sub> dissolving at a high RH that is still lower than where CaCO<sub>3</sub> dissolves. In

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fact your humidograms present evidence for this (Fig. 8), but it is not discussed.

What thermodynamic implications does this the production of solid  $\text{Ca}(\text{HCO}_3)_2$  present? How might the existence of this thermodynamically inhibited or even forbidden state be explained?

Response (part 5): We thank for the reviewer's advice. In the revised manuscript we have interpreted and discussed the HTDMA humidograms and CCN activity in more detail and included the implication of support for the  $\text{Ca}(\text{HCO}_3)_2$  (s). We have substantially modified the last paragraphs of the section 3.4 beginning on p. 15 line 2.

We believe that discussion and explanation of thermodynamic implications of the thermodynamically inhibited or even forbidden state  $\text{Ca}(\text{HCO}_3)_2$ (s) is beyond the scope of this manuscript. Although we formulated the hypothesis of existence of  $\text{Ca}(\text{HCO}_3)_2$ (s) now more clearly, we underlined that for us it is still a hypothesis.

General comments (part 6) The paper does not discuss the possible formation of carbonic acid, an important intermediate in reactions of  $\text{CaCO}_3$  with acidic gases (Al-Hosney and Grassian, 2004). As carbonic acid,  $\text{H}_2\text{CO}_3$ , is only stable adsorbed on particle surfaces under dry conditions, this could explain some of the observations in the dry chamber experiments that are currently attributed to calcium bicarbonate. Vibrational spectroscopy is the best analytical method to distinguish between carbonate, bicarbonate, and carbonic acid. Was this method available in your experiments?

Response (part 6): As mentioned above the conditions of drying of the laboratory and the chamber aerosol is similar. There is no reason to assume that aerosols in the chamber are different from those generated in the small scale laboratory study.

Al-Hosney and Grassian, 2004 worked at conditions significantly different from ours, applying mbars of  $\text{HNO}_3$  to generate carbonic acid from calcite. Carbonic acid appeared as surface layers and was unstable towards water as stated by Al-Hosney and Grassian, 2004 : "Carbonic acid is stable on the surface in the absence of water at

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298 K. However, theoretical calculations have shown that carbonic acid is significantly destabilized even in the presence of only one water molecule and rapidly dissociates to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . (Loerting, T.; Tautermann, C.; Kroemer, R. T.; Kohl, I.; Hallbrucker, A.; Mayer, E.; Leidl, K. R. *Angew. Chem., Int. Ed.* 2000, 39, 892.)". It is therefore unlikely that carbonic acid is formed in our dry chamber experiments at RH 5% and 1 ppb  $\text{HNO}_3$  background. Carbonic acid may be formed in traces by the minimal uptake of  $\text{HNO}_3$  in our dry chamber experiment. In any case traces of carbonic acid adsorbed at the surfaces cannot explain the high amount of  $\text{CO}_2$  evaporating out of the bicarbonate aerosols at the temperature of  $300^\circ\text{C}$  of the QAMS vaporizer. We have added a line discussion of carbonic acid in the revised manuscript (p. 20, line 15):

"Due to the low  $\text{HNO}_3$  background and the residual 5% RH, we exclude the formation of significant amounts of surface adsorbed carbonic acid as observed by Al-Hosney and Grassian (2004) at much larger  $\text{HNO}_3$  partial pressures."

We did not carry out IR spectroscopic studies.

General comments (part 7) On a related note, there was no discussion of possible metastable hydrate precipitates of  $\text{CaCO}_3$  in the generated particles; three are known to exist (Brecevic and Kralj, 2007).

Response (part 7): As mentioned above the conditions of drying of the laboratory and the chamber aerosol is similar. There is no reason to assume that aerosols in the chamber are different from those generated in the lab. Precipitation of metastable  $\text{CaCO}_3$  hydrates can be excluded, as the crystal water would be detected by AMS. Observed stoichiometric ratios of  $\text{CO}_2/\text{H}_2\text{O}$  and the absence of excess water excluded the formation of hydrates. We added in the revised manuscript (p. 13, line 21):

" Moreover, because of the  $\text{H}_2\text{O}/\text{CO}_2$  stoichiometry in cases 1 and 3 (Fig.7 b) and the absence of excess water (Fig. 7b, c), we can rule out inclusions of aqueous phase and the formation of metastable  $\text{CaCO}_3$  hydrates as described e.g. in Gmelin (1961, p. 937f) or by Brecevic and Kralj (2007)."

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General comments (part 8) The long chamber experiments under wet and dry conditions prevent further evidence that  $\text{CaCO}_3(\text{s})$  particles are produced when  $\text{Ca}(\text{HCO}_3)$  particles are annealed, but this is not presented clearly. The fact that the supposed  $\text{CaCO}_3$  particles only uptake substantial nitrogen oxides to produce particulate nitrate under humid conditions is in agreement with previous studies which have found the reaction of  $\text{CaCO}_3(\text{s}) + \text{HNO}_3(\text{g})$  to be limited to the surface layers under dry conditions.

Response (part 8): We don't understand this comment. Why do our chamber experiments prevent evidence that " $\text{CaCO}_3(\text{s})$  particles are produced when  $\text{Ca}(\text{HCO}_3)$  particles are annealed?"

The aerosol chamber was at ambient temperature, no annealing was involved here. The expectation is that  $\text{Ca}(\text{HCO}_3)_2(\text{aq})$  is converted to  $\text{CaCO}_3(\text{s})$  already at room temperature as soon as the particles are drying. The dry chamber experiments were performed in order to allow for more time for the conversion of  $\text{Ca}(\text{HCO}_3)_2$  to  $\text{CaCO}_3(\text{s})$ , since we first speculated that the time scales in the lab experiments were possibly too short for this conversion.

We have referred to the paper by Vlasenko et al. (2009) in discussing the aging process of  $\text{Ca}(\text{HCO}_3)_2/\text{CaCO}_3$  in the dry chamber in presence of  $\text{HNO}_3$  in the revised manuscript (p.20, line 22):

"Such a surface to bulk kinetic constrain was suggested before by Vlasenko et al. (2009) for the reaction of nitric acid dust with Arizona Test Dust."

General comments (part 9) Under moist conditions this reaction is facilitated by the dissolution of the  $\text{Ca}(\text{NO}_3)_2$  product, allowing successive layers of  $\text{CaCO}_3$  to react with  $\text{HNO}_3$ . Please be more explicit in discussing this and the "protective coating" you infer.

Response (part 9)

In the original manuscript we described this already explicitly (p. 8029 , l. 8 ):

C5837

"These observations demonstrated that a substantial heterogeneous conversion into the more soluble  $\text{Ca}(\text{NO}_3)_2$  occurred. We suggest that in early stages of the experiment this took only place on the surface of the particles. But since the nitrate is much more hygroscopic than both, carbonate and bicarbonate, the particles took up water forming a concentrated solution on the surface (Krueger et al., 2003). This further increased the uptake of  $\text{HNO}_3$  which is larger on wet particles (Liu et al., 2008a) and also dissolved the upper layers of carbonate. The conversion of  $\text{Ca}(\text{HCO}_3)_2$  to  $\text{Ca}(\text{NO}_3)_2$  thus was accelerated and the reaction of bicarbonate to carbonate was promoted as no protective layer was formed. Carbonate/bicarbonate decreased as the reaction proceeded but were not completely depleted over the time period of the chamber experiment. Therefore the hygroscopic growth was lower than that of pure nitrate. The droplet activation of chamber particles at the final stages was only slightly less than that of pure  $\text{Ca}(\text{NO}_3)_2$  as the reaction to nitrate was much faster than that conversion to carbonate."

We agree that the phrase of the "protective layer" fell too short. We referred here to our suggestion in context of the experiments in the dry chamber (p.8028, l. 5). (But see also comments below.) Here possibly a  $\text{CaCO}_3(\text{s})$  layer was formed on the surface of the particles, which protected the  $\text{Ca}(\text{HCO}_3)_2$  core. Due surface to bulk kinetic constrain (Vlasenko et al. 2009, see above) this layer seems to be stable even in the presence of small amounts of  $\text{HNO}_3$  in the dry chamber. We reformulated accordingly (p. 21, line 25 ):

"The conversion of  $\text{Ca}(\text{HCO}_3)_2$  to  $\text{Ca}(\text{NO}_3)_2$  thus was accelerated and the reaction of bicarbonate to carbonate was promoted as no protective layer of  $\text{CaCO}_3(\text{s})$  could be formed as suggested for the dry chamber case."

General comments (part 10) It would be beneficial if similar AMS data for  $\text{CO}_2^+$  and  $\text{NO}_3^-$  presented in Fig. 12 were shown for a long chamber experiment run under dry conditions, in addition to the humid experiment presented.

C5838



Response (part 10):

We did not operate the AMS on the first dry experiment. During the second dry experiment we had an 11h overnight failure of the AMS during the experiment. Therefore we have only data from the very beginning and the very end of the experiment. From those we extracted the initial and the final compositions as given in the manuscript.

General comments (part 11) The analysis of the hygroscopic growth and CCN activation measurements is incomplete and requires further development. First the data is often described in a qualitative (see examples below) and not quantitative manner, this must be amended. It would be most beneficial if the data was also converted to one of the commonly used hygroscopicity parameters (e.g. Petters and Kreidenweis, 2007; Rissler et al., 2006; Wex et al., 2007), to allow quantitative comparisons to be made within this dataset and with others. Figure 9 should be plotted using a log-log scale, so that the linear trends in the SS-Dcrit data pairs can be better evaluated to determine if particle hygroscopicity is constant across dry particle sizes.

Response (part 11): Agreed. We have extended the discussions in the Hygroscopic Growth sections (3.4, p. 15, line 2) and the CCN section (3.5, p. 17, line 5) in the revised manuscript. Analysis by one parameter Köhler approach applying the hygroscopicity parameter kappa was performed. Based on kappa our HG and CCN data are now compared to each other and to observations in the literature. The Figure 9 was changed as proposed.

General comments (part 12) The "expected" hygroscopic properties of  $\text{Ca}(\text{HCO}_3)_2$  are often mentioned yet never stated, what are they? If Köhler theory was used to calculate them what thermodynamic properties and assumptions were used? Of particular importance are the physical phase and solubility assumed for  $\text{Ca}(\text{HCO}_3)_2$  under sub-saturated and supersaturated conditions. For example, what is the expected/predicted activation diameter at  $\text{SS} = 0.2\%$  for pure  $\text{Ca}(\text{HCO}_3)_2$ , and does this agree with the observations?

C5839

Response (part 12): We don't understand this comment. We searched the manuscript for the phrase "expected". It was used several times, but we never referred to "expected" hygroscopic properties of  $\text{Ca}(\text{HCO}_3)_2$  in general. In the chamber section 3.6, we compared the observations in the chamber a few times to our expectation based on our small scale laboratory study. We clarified that in the revised manuscript (p. 20, line 28):

"In the humid chamber (flushed with particle free outside air) Dcrit at 0.2 % SS reached 135 nm ( $\kappa=0.14$ ) within the first 15 min (blue curve in Fig. 10) which agreed well with  $\text{Ca}(\text{HCO}_3)_2$ (s) from our laboratory study (see above)."

General comments (part 13) How certain are you that the TEM images of the dried atomized  $\text{Ca}(\text{HCO}_3)_2$  particles before and after annealing indicate that the particles were solid? Could any deformation of the spherical particles be caused by the TEM tip? The features shown in the TEM images could also be interpreted as patches of liquid on the surface.

Response (part 13): The particles shown in Fig.6 look like solid spheres to us. They are in any case solid structures as they don't wet the supporting surface. To us they look more like having internal structures or dimples.

The abbreviation TEM was introduced too late in the manuscript, it means Transmission Electron Microscopy. This was changed in revised manuscript. In the TEM study no tips are involved that could have caused deformation of the particles.

General comments (part 14) Finally, this method is presented as a "simple" new way to generate relatively pure  $\text{CaCO}_3$  aerosol. I must object to this characterization as the described method is somewhat complicated, and potentially limited. First some time is required to prepare the saturated  $\text{Ca}(\text{HCO}_3)_2$  solution. A 300 C tube furnace is also required to convert  $\text{Ca}(\text{HCO}_3)_2$  to  $\text{CaCO}_3$ , which is not commonly available in most aerosol labs. Most importantly, based on the CCN activation results presented in Fig. 9, the  $\text{CaCO}_3$  particles generated here are slightly more hygroscopic than those reported

C5840

by Sullivan et al. (2009b), suggesting that the Sullivan et al. method produced particles with chemical properties more similar to those expected from pure calcite. Therefore I must conclude that the dry dispersion method of Sullivan et al. is both simpler and produces particles with more desirable properties than the method used here. Also, what other mineral particle systems can be generated by this method, or is it restricted to just CaCO<sub>3</sub>? This is not to imply this new method does not have merit or that the findings regarding solid Ca(HCO<sub>3</sub>)<sub>2</sub> particles are not valuable, but I do not believe it presents a new highly viable mineral particle generation method. One advantage of this method is it may produce more stable particle concentrations over periods of hours at particle sizes required for hygroscopic growth and CCN activation studies compared to dry dispersion methods. If true this could be stated in the manuscript.

Response (14): It is debatable if a dry-bed dispersion is simpler and generally more accessible to aerosol labs than the method proposed by us. We will nevertheless cancel the word "simple" in the revised manuscript. We underline, that CaCO<sub>3</sub>(s) generated by our method is systematically somewhat more CCN-active, but still agrees within the errors with CaCO<sub>3</sub>(s) of Sullivan 2009b produced by dry-bed dispersion (Fig. 9). We plan to extend the method to other mineral particle systems.

#### Specific Comments

Comment: Abstract: "Experiments in the Large Jülich Aerosol Chamber showed that Ca(HCO<sub>3</sub>)<sub>2</sub> can exist for several hours under dry atmospheric conditions which is in contrast to the current believe that Ca(HCO<sub>3</sub>)<sub>2</sub> is unstable in the atmosphere." This is a prime example of the vague descriptions of the results. Do you conclude that SOLID Ca(HCO<sub>3</sub>)<sub>2</sub> can exist for several hours under dry conditions? Aqueous Ca(HCO<sub>3</sub>)<sub>2</sub> is stable (as its dissociated ions).

Response: We referred to solid Ca(HCO<sub>3</sub>)<sub>2</sub> here. But we also suggested now that it may be enclosed in a CaCO<sub>3</sub>(s) mantle. In the revised manuscript, we have specified the physical states of the aerosols. (See also response to general comments.) We

C5841

reformulated larger parts of the abstract in the revised manuscript (p. 1, line 23):

"The dried Ca(HCO<sub>3</sub>)<sub>2</sub> particles were somewhat more hygroscopic than CaCO<sub>3</sub> particles. However, during humidification a restructuring took place and ~2/3 of the Ca(HCO<sub>3</sub>)<sub>2</sub> was transformed to CaCO<sub>3</sub>. The mixed Ca(HCO<sub>3</sub>)<sub>2</sub>/CaCO<sub>3</sub>(s) particles were insoluble with a growth factor of 1.03 at 95% (hygroscopicity parameter  $\kappa=0.011\pm0.007$ ) relative humidity. This compares to a corresponding growth factor of 1.01 for CaCO<sub>3</sub>(s) ( $\kappa=0.0016\pm0.0004$ ). Mass spectrometric composition analysis, restructuring, and insolubility of the mixed particles suggested that solid Ca(HCO<sub>3</sub>)<sub>2</sub>(s) was observed. This would be in contrast to the current believe that Ca(HCO<sub>3</sub>)<sub>2</sub>(s) is thermodynamically instable. The CCN activity of Ca(HCO<sub>3</sub>)<sub>2</sub>(s) aerosol ( $\kappa\approx0.15$ ) is remarkably higher than that of CaCO<sub>3</sub> aerosol ( $\kappa=0.0019\pm0.0007$ ) and less than that of Ca(NO<sub>3</sub>)<sub>2</sub>. The noticeable but limited solubility of Ca(HCO<sub>3</sub>)<sub>2</sub> of  $\approx0.001$  mol/l explains limited hygroscopic growth and good CCN activity.

Experiments in the Large Jülich Aerosol Chamber indicated that Ca(HCO<sub>3</sub>)<sub>2</sub>(s) can exist for several hours under dry atmospheric conditions. However, it is likely buried in a protective layer of CaCO<sub>3</sub>(s)."

Comment: P. 8011, line 27: "However, most of the mineral dust components are characterized by very low solubility which makes atomization from solution difficult." An important related issue to mention is that placing insoluble pure or natural mineral powders into water has been observed to cause large changes in their hygroscopic properties (Herich et al., 2009; Koehler et al., 2009; Koehler et al., 2007). For the CaCO<sub>3</sub> system, et al. (2009b) reported that particles atomized from a mixture of calcite in water produced particles that were up to 100 times more hygroscopic than when the same powder was dispersed dry.

Response: Sullivan et al. (2010) reported that for the sub-100nm wet-dispersed Solvay CaCO<sub>3</sub> particles the  $\kappa$  is 100 times higher than that from the dry-dispersed Solvay CaCO<sub>3</sub> particles. From the high CCN activity found Sullivan et al. (2010) conclude

C5842

that “the particles would have had to be composed of  $\geq 20\%$  by volume of a soluble contaminant with  $\kappa_{app} \geq 0.5$  (similar to many inorganic salts (Sullivan et al. 2009b)) to exhibit  $\kappa_{app} \geq 0.1$ ”. They further report “the solubilities of the known calcium carbonate hydrates, and calcium hydroxide, are not sufficient to produce apparent hygroscopicities large enough to explain the observed hygroscopicity”. At the same time, the morphology of sub-100 nm particle (Fig 7 therein) is very similar to the result of our study. Maybe the high CCN activity was caused by the formation of some  $\text{Ca}(\text{HCO}_3)_2$ , whose CCN activity is high according to our study?

We added in the introduction (p. 3, line 31):

"Moreover, it was observed by several groups that mineral particles generated by spray-drying of suspension are more hygroscopic than those from dry beds (Herich et al., 2009, Koehler et al., 2007, 2009, Sullivan et al. 2010). Sullivan et al. (2010) reported that for sub-100nm wet-generated  $\text{CaCO}_3$  particles the hygroscopicity parameter  $\kappa$  is 100 times larger than that from the dry bed generated  $\text{CaCO}_3$  particles."

And in section 3.5 (p. 17, line 21):

Wet-processed water-insoluble or mineral particles often exhibit a severely enhanced hygroscopicity and cloud droplet activation compared to dry processed particles (Herich et al., 2009, Koehler et al., 2007, 2009, Sullivan et al. 2010). Sullivan et al. (2010) reported a  $\kappa$  of 0.1 for wet-dispersed  $\text{CaCO}_3$  compared to  $\kappa_{\text{CO}_3} = 0.0011$  of dry-dispersed  $\text{CaCO}_3$  aerosols. Considering this huge difference of a factor of 100 in  $\kappa$ , the small difference within the errors between the  $\text{CaCO}_3$  aerosol generated by the presented method and the dry-dispersed of Sullivan are negligible. We conclude that our  $\text{CaCO}_3$  aerosol is of sufficient quality as required by hygroscopicity and CCN studies.

Comment: Was the  $\text{CaCO}_3/\text{Ca}(\text{HCO}_3)_2$  solution itself ever characterized? This would be a better method to determine the timescale required to approach equilibrium than the indirect measurement through the particle number concentration and size.

C5843

Response: The  $\text{Ca}(\text{HCO}_3)_2$  solutions itself were not directly characterized. We agree that this would be the better method. However, our indirect method served the purpose as we were interested in stability and reproducibility of the aerosol generation.

Comment: Sec. 2.4: The HTDMA operation description is missing some details. I assume the second DMA's voltage was scanned or stepped to measure the humidified aerosols' size distribution with a CPC? Please state the sample and sheath flows used in the various DMAs.

Response: We added the details about the HTDMA to the revised manuscript.

Comment: Sec. 2.6: In addition to background  $\text{HNO}_3(\text{g})$  were any other acids detected, such as  $\text{HCl}(\text{g})$ ?

Response: The chamber was usually used for the studies of nitrogen oxides.  $\text{HCl}$  or  $\text{NaCl}$  were never used in this chamber. Therefore, only nitrate was detected in the stripping solution.

Comment: It is important to point out that the dry synthetic air had low (please state) concentrations of  $\text{CO}_2$ , while the filtered outdoor air had atmospheric levels of  $\text{CO}_2$ . Please list the  $[\text{CO}_2]$  for all experiments.

Response: We used dry synthetic air (Linde LiPur, quality 6.0, 99.9999%) in all experiments, but the single one with outside air. This was stated in section 2.6 (P8018 line 15). We added new Table 5 with experimental conditions to the revised manuscript. In addition we highlighted the fact that the experiment with outside air contained  $\text{CO}_2$  in section 2.6 and in the figure caption of figure 10.

Comment: The unexplained result of the AMS collection efficiency appearing to be 100% for the Case 4 experiment, instead of 50% in the other Cases, could be further investigated by sampling a suspended dry commercial calcite powder. Was or could this be tested?

Response: This is a good idea, but one has to consider that the particle beam is

C5844

widened in addition, if the particles are not spherical. This can also reduce the collection efficiency and dispersion of the particle beam is used by the AMS community to test for crystalline particles. Moreover, we don't have a dry bed generator in our lab, so we did not perform the test.

Comment Sec. 3.6: Please state the RH values for the dry and humid chamber experiments.

Response: The RH values for the chamber studies have been stated in the experimental part (P8018 line 10, 13, 16, 18), and is <3%RH in the prepared chamber and <5% (<3%+2%) after the aerosol was added. For the humid chamber experiments RH=40%. RH is now given in new Table 5 in the revised manuscript.

Comment P.8026, line 2 (and elsewhere): Be sure to state the supersaturation at which the Dcrit values were determined in all cases. Including a Table of the SS-Dcrit data pairs from the various experiments would be most useful.

Response: In all chamber studies the SS was adjusted to 0.2 % SS. In the chamber experiments p. 8027, 1§the SS was partly missing, however always 0.2 % SS as stated in the figure caption of fig 10. We added the missing SS in the revised manuscript.

We also added the new Table 4 with the SS-Dcrit data pairs from our laboratory study.

Comment P. 8027, line 11: At SS 0.20%, Dcrit = 130 nm ( $\kappa = 0.16$ ) is more than twice as hygroscopic than Dcrit = 170 nm ( $\kappa = 0.069$ ) when converted to a hygroscopicity parameter (Petters and Kreidenweis, 2007). Thus the qualitative description of "somewhat higher" given does not seem appropriate here. For the "pure" CaCO<sub>3</sub> with Dcrit= 150 nm at SS = 0.85%, this corresponds to  $\kappa = 0.0028$ . Sullivan et al. (2009b) reported  $\kappa = 0.0011 - 0.0004$  for CaCO<sub>3</sub>.

Response: We agree with the referee and will report kappas in addition. However, the kappa reported by Sullivan et al. 2009b for Dcrit = 150 nm was 0.0018, outside the stated range and only 30% smaller than ours.

C5845

Comment P. 8027, line 27: The addition of 2-4% NO<sub>3</sub> (as Ca(NO<sub>3</sub>)<sub>2</sub>,  $\kappa = 0.5$  from Sullivan et al., (2009b)) can have a significant effect on the particle's resulting hygroscopicity, particularly if the particles are originally composed of weakly hygroscopic components. Thus this small amount of 2-4% NO<sub>3</sub>- detected in the chamber particles can have a significant effect on the particle's hygroscopicity.

Response: This is correct. Although we are converting from bicarbonate to carbonate, thus making the particle less hygroscopic we are far away from pure CaCO<sub>3</sub> this is not only due to HCO<sub>3</sub><sup>-</sup> but also due to the presence of nitrate. We stated that more clearly in the revised manuscript (p. 20, line 5).

"Therefore besides residual Ca(HCO<sub>3</sub>)<sub>2</sub>, also Ca(NO<sub>3</sub>) must have contributed to the enhanced GF and the enhanced CCN activity and of the particles after 14h."

Comment P. 8028, line 24: The authors propose that the Ca(HCO<sub>3</sub>)<sub>2</sub> slowly converted to CaCO<sub>3</sub> in the dry CO<sub>2</sub>-free chamber. They state this could explain the observed decrease in hygroscopicity which does not become as CCN-inactive as expected for pure CaCO<sub>3</sub>. This is only valid if the hygroscopic properties of Ca(HCO<sub>3</sub>)<sub>2</sub> and CaCO<sub>3</sub> are different under supersaturated conditions. This would likely require that Ca(HCO<sub>3</sub>)<sub>2</sub> and CaCO<sub>3</sub> dissolve at different water activities. Evidence for this is presented in the humidograms (Fig. 8) but their interpretation is incomplete. Please clarify these important issues. In the dry chamber the authors state that ~40% of the particle remained Ca(HCO<sub>3</sub>)<sub>2</sub>. Does the predicted hygroscopicity of a 40% Ca(HCO<sub>3</sub>)<sub>2</sub> and 60% CaCO<sub>3</sub> particle match the observed hygroscopicity? More quantitative analysis is required here.

Response: We use now  $\kappa$  for comparison in the revised manuscript. The hygroscopicity parameters  $\kappa = 0.1/0.07$  for aerosol in the dry chamber were smaller than  $\kappa \approx 0.15$  observed for the mixed CaCO<sub>3</sub>/Ca(HCO<sub>3</sub>)<sub>2</sub>(s) from the laboratory study. This is stated in the revised manuscript (see also comments above).

Since the particles were solid it is difficult to apply mixing rules, since particle morphol-

C5846

ogy may play a role (CaCO<sub>3</sub> coating!). No further changes were implemented in the revised manuscript.

Comment: P. 8028, line 6: (R1) produces Ca(HCO<sub>3</sub>)(aq). How would this AQUEOUS reactive alkaline component “protect” the particle bulk from further reaction with HNO<sub>3</sub>(g)? It should in fact have the opposite effect; an aqueous layer would allow HNO<sub>3</sub> to react with successively deeper layers of the particle. Your evidence of enhanced nitrate uptake and the associated increase in hygroscopicity in the humid versus dry chamber experiments is evidence for the inhibition of HNO<sub>3</sub> uptake. This has been observed in other studies and is attributed to the lack of formation of aqueous intermediates and products at the particle surface under dry conditions. Again please clarify what physical state you propose the particle component(s) existed in.

Response: We are sorry that this is a typo error. It should be R2 here instead of R1. We have corrected it in the revised manuscript and have discussed the inhibition of HNO<sub>3</sub> uptake in the dry chamber (see above).

Comment: P. 8028, line 14: Explain what the “expected value” for Dcrit is and how it was derived. Again, state the SS that these Dcrit were measured at.

Response: Accepted and changed accordingly. (see also general comments)

Comment: Sect. 3.6: The interpretation of the chamber experiment observations would be more convincing if an experiment in which NO<sub>x</sub> and O<sub>3</sub> was added to the chamber under dry conditions was also performed, to test if the particles are converted to nitrate or not.

Response: We agree with the referee that more experiments are always better. However, the dry experiments served to investigate the persistence of Ca(HCO<sub>3</sub>)<sub>2</sub>. We show that HNO<sub>3</sub> uptake at the low background concentration is slow. We measured the composition at the beginning and at the end of the dry experiment by AMS. That was sufficient for our purposes. Heterogeneous chemistry was not in the focus of this

C5847

manuscript.

Comment: P. 8028, line 20: As you know or can estimate the concentration of HNO<sub>3</sub> in the chamber, and know the exposure time, you can compare your observed rate of conversion for the CaCO<sub>3</sub>/Ca(HCO<sub>3</sub>)<sub>2</sub> particles to Ca(NO<sub>3</sub>)<sub>2</sub> with that presented in Sullivan et al.(2009a); how do they compare?

Response: Again we were interested in the long term persistence of our aerosols, here especially of the Ca(HCO<sub>3</sub>)<sub>2</sub>(s), generated by our new method. The wet chamber experiments served to simulate their behavior under conditions more realistic to the ambient than the dry experiments. Heterogeneous conversion of CaCO<sub>3</sub> with HNO<sub>3</sub> is not the purpose of this study. The experiments were not optimized for this purpose, for which we would have added a known amount of HNO<sub>3</sub> directly. HNO<sub>3</sub>(g) in the chamber was not measured during the experiments.

Comment: P. 8029, line 2: Please be quantitative instead of saying “a little Ca(HCO<sub>3</sub>)<sub>2</sub>” and “a significant CaCO<sub>3</sub> fraction”.

Response: In revised manuscript, the relative content of 6% is stated.

Comment: P. 8028, line 28: What was the AMS nitrate signal response during the dry chamber experiments?

Response: The noise equivalent level was better than 0.05 ug/m<sup>3</sup>, the signal levels were 0.25 ug/m<sup>3</sup> in the beginning and 0.4 ug/m<sup>3</sup> at the end of the dry experiment.

Comment: P. 8029, line 9: The suggestion that the conversion to Ca(NO<sub>3</sub>)<sub>2</sub> facilitates further reaction with HNO<sub>3</sub> because it is more hygroscopic is not strictly correct. It is the higher solubility of Ca(NO<sub>3</sub>)<sub>2</sub> versus CaCO<sub>3</sub> which facilitates further reaction of CaCO<sub>3</sub> with HNO<sub>3</sub>(g), as Ca(NO<sub>3</sub>)<sub>2</sub> will deliquesce  $\sim$ 10% RH. You state that this also explains why Ca(NO<sub>3</sub>)<sub>2</sub> facilitates the reaction while Ca(HCO<sub>3</sub>)<sub>2</sub> does not. Are you assuming that Ca(HCO<sub>3</sub>)<sub>2</sub> is always solid in this discussion?

Response: We agree that the reaction was facilitated because of the solubility of

C5848

Ca(NO<sub>3</sub>)<sub>2</sub> whose deliquescence introduced water promoting the reaction to the bulk of the particle. This was stated already on p. 8029, l. 7 (old manuscript):

"These observations demonstrated that a substantial heterogeneous conversion into the more soluble Ca(NO<sub>3</sub>)<sub>2</sub> occurred."

We have nevertheless underlined the solubility aspect one more time in the manuscript (p. 21 line 21).

We don't know the state of Ca(HCO<sub>3</sub>)<sub>2</sub> in the wet experiments, since there is water taken up by the particles. It may well be that the 6% bicarbonate after 23h survived in the inner core of the particles as a solid as there is still also 30% CaCO<sub>3</sub> around. Growth factors at 40%RH were 1.1-1.2 for the nitrate processed particles (Fig.11).

Comment: P. 8029, line 15: Again Ca(HCO<sub>3</sub>)<sub>2</sub>(aq) as a protective layer does not make sense. If you believe Ca(HCO<sub>3</sub>) forms a solid layer under dry conditions that is less reactive than CaCO<sub>3</sub>(s), this must be explicitly stated. (R1) shows Ca(HCO<sub>3</sub>)<sub>2</sub>(aq) as the product, so this is contradictory. Again, the role of carbonic acid must also be considered.

Response: As mention in the responses above, we are sorry, but (R1) was an error in the old manuscript. It should be R2 here instead of R1. We meant solid CaCO<sub>3</sub> as a protective layer under dry condition. We have corrected it in the revised manuscript.

Carbonic acid is unimportant in our system compare AlHosney and Grassian, 2004, p.8086 However, theoretical calculations have shown that carbonic acid is significantly destabilized even in the presence of only one water molecule and rapidly dissociates to CO<sub>2</sub> and H<sub>2</sub>O. From these theoretical results, it is reasonable to expect that adsorbed carbonic acid would dissociate on the surface in the presence of adsorbed water. (see also general comments)

Comment: The fact that large amounts of nitrate uptake were observed in the humid experiments while little was uptake occurred in the dry experiments clearly suggests

C5849

the role of differing surface chemistry under wet versus dry conditions, but this is not explained convincingly or clearly here.

Response: Unexpected persistence of Ca(HCO<sub>3</sub>)<sub>2</sub> was addressed of the paper. Regarding the purpose of our paper we proposed mechanisms and processes (p. 20, line 7 and p. 21, line 19) that explained the different persistence in the wet and the dry chamber under consideration that we were not free of HNO<sub>3</sub> in the chamber. After removing the error with R1 and R2 this should be clearer now. We agree heterogeneous chemistry is interesting, but beyond the purpose and scope of the presented manuscript.

Comment: P. 8029, line 18: "The droplet activation of chamber particles at the final stages was only slightly less than that of pure Ca(NO<sub>3</sub>)<sub>2</sub> as the reaction to nitrate was much faster than that conversion to carbonate." This sentence does not make sense, please clarify and be specific.

Response: We modified this sentence as (p. 21, line 29)

"The  $\kappa=0.45$  for droplet activation of chamber particles at the final stages was only 10% less than that of pure Ca(NO<sub>3</sub>)<sub>2</sub> as the reaction to nitrate was much faster than that conversion to carbonate."

Comment: Conclusions: Be quantitative in describing the differences in CCN-activity of the various systems, instead of saying "a little less active", "much better", etc.

Response: In many instances we use kappa now to describe quantitatively.

Comment: Table 3: Does "calc." refer to that estimated from the SMPS measurements? In what columns has the normalization been applied?

Response: Calc means the expectation value calculated from the composition obtained in Table 2. In the "Measured mn(CO<sub>2</sub>)" and "Measured mn(H<sub>2</sub>O)", the normalized has been applied. We have stated this now in the subscript of Table 3 in the revised manuscript.

C5850

Comment: Table 4: If this is for the long chamber experiments please specify this. Why not also include the GF data for the dry chamber experiment?

Response: Table 4 is for the humid chamber experiment with NO<sub>x</sub> added, this was specified now in the revised manuscript. As shown in Figure 11 the growth factors in the dry chamber experiments don't change much in time. So we prefer to omit it from Table 4. In the revised manuscript Table 4 became Table 6.

Comment: Figure 1 is not necessary.

Response: Figure 1 will help the reader understand the setup easily. It also makes clear that the aerosol were always dried before analysis.

Comment: Figure 2: Include the size distribution of the dried aerosol? To what RH was the atomized aerosol dried after one diffusion drier?

Response: This is the size distribution of the aerosol generated from spraying Ca(HCO<sub>3</sub>)<sub>2</sub> solutions and drying the aerosol to <5%RH. In the revised manuscript this now stated clearly.

Comment: Figure 9: Plot in log-log space to reveal the expected linear relationships between log SS and log Dcrit.

Response: Done.

Comment: Fig. 10: The figure caption should indicate when CO<sub>2</sub> was or wasn't present.

Response: Done. See also response above.

Comment: Fig. 11: I see only two different blue colors, not three. What is the green symbol? State the RH for the dry and humid experiments.

Response: The Fig.11 was changed accordingly.

Technical Corrections

C5851

Comment: Abstract, line 16: "believe" should be "belief".

Response: corrected.

Comment: P. 8017, line 12: "pretends" is not an appropriate word.

Response: It was modified to "contributes to activation"

Comment: P. 8018, line 8: Typo: "the rise RH".

Response: corrected.

Comment: P. 8029, line 6: "Nitrate and water uptake and overcompensated the chamber losses (Fig.12)." There is a typo here and the meaning is not clear.

Response: It has been modified to (p. 21, line 17): "Nitrate and water uptake overcompensated the decrease of aerosol volume concentration due to losses to the chamber walls (Fig.12)."

Comment: Fig. 4: Please change the x-axis numbers to read 100, 200, 300, : : :

Response: Done.

Comment: Fig. 6: Why is the contrast so different between the left and right figures? Unless this is necessary please make them the same to facilitate comparison of features.

Response: The two images are the raw images obtained by TEM. The only difference a is slightly different magnification factor of 100 000 and 78 000, respectively. In our opinion, the contrast does not really prevent distinguishing the difference of the particles before and after annealing. We cannot change the contrast easily, so we would like to keep the images as they are obtained.

Comment: Fig. 7: Y-axis labels are too small and difficult to read.

Response: In the revised manuscript, Y-axis label are shown larger.

C5852

Comment: Fig. 9: Make the symbol color scheme match that of Fig. 8 (middle and light blues are different).

Response: Done.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 8009, 2010.

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