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Interactive comment on “Novel method of generation of $\text{Ca}(\text{HCO}_3)_2$ and CaCO_3 aerosols and first determination of hygroscopic and cloud condensation nuclei activation properties” by D. F. Zhao et al.

Anonymous Referee #2

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General Comments

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

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gestions 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.

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 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.

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?

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.

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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 $\text{Ca}(\text{HCO}_3)_2$ 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 $\text{Ca}(\text{HCO}_3)_2$ 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 $\text{CaCO}_3(\text{s})$. Can the properties of $\text{Ca}(\text{HCO}_3)(\text{s})$ explain this, or does it indicate contamination by more soluble hygroscopic compounds?

For example, in the Abstract you state, “Fresh $\text{Ca}(\text{HCO}_3)_2$ particles are somewhat more hygroscopic than CaCO_3 particles although both have small growth factors of 1.03 and 1.01, respectively, at 95% relative humidity. The CCN activity of $\text{Ca}(\text{HCO}_3)_2$ aerosol is remarkably higher than that of CaCO_3 aerosol and only slightly less than that of $\text{Ca}(\text{NO}_3)_2$.” Why is $\text{Ca}(\text{HCO}_3)_2$ nearly as hygroscopic as $\text{Ca}(\text{NO}_3)_2$ above water saturation but nearly non-hygroscopic at 95% RH? $\text{Ca}(\text{NO}_3)_2$ should exhibit a much larger GF than 1.03 at 95% RH. This could be explained by $\text{Ca}(\text{HCO}_3)$ dissolving at a high RH that is still lower than where CaCO_3 dissolves. In 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?

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The paper does not discuss the possible formation of carbonic acid, an important intermediate in reactions of CaCO_3 with acidic gases (Al-Hosney and Grassian, 2004). As carbonic acid, H_2CO_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?

On a related note, there was no discussion of possible metastable hydrate precipitates of CaCO_3 in the generated particles; three are known to exist (Brecevic and Kralj, 2007). 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 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. Under moist conditions this reaction is facilitated by the dissolution of the $\text{Ca}(\text{NO}_3)_2$ product, allowing successive layers of CaCO_3 to react with HNO_3 . Please be more explicit in discussing this and the “protective coating” you infer.

It would be beneficial if similar AMS data for CO_2^+ and NO_3^- presented in Fig. 12 were shown for a long chamber experiment run under dry conditions, in addition to the humid experiment presented.

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

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the SS-Dcrit data pairs can be better evaluated to determine if particle hygroscopicity is constant across dry particle sizes.

The “expected” hygroscopic properties of $\text{Ca}(\text{HCO}_3)_2$ are often mentioned yet never stated, what are they? If Kohler 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 subsaturated 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?

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.

Finally, this method is presented as a “simple” new way to generate relatively pure 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 CaCO_3 , which is not commonly available in most aerosol labs. Most importantly, based on the CCN activation results presented in Fig. 9, the CaCO_3 particles generated here are slightly more hygroscopic than those reported 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_3 ? This is not to imply this new method does not have merit or that the findings regarding solid $\text{Ca}(\text{HCO}_3)_2$ 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.

Specific Comments

Abstract: “Experiments in the Large Julich Aerosol Chamber showed that $\text{Ca}(\text{HCO}_3)_2$ can exist for several hours under dry atmospheric conditions which is in contrast to the current believe that $\text{Ca}(\text{HCO}_3)_2$ is unstable in the atmosphere.” This is a prime example of the vague descriptions of the results. Do you conclude that SOLID $\text{Ca}(\text{HCO}_3)_2$ can exist for several hours under dry conditions? Aqueous $\text{Ca}(\text{HCO}_3)_2$ is stable (as its dissociated ions).

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_3 system, Sullivan 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.

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.

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.

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

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It is important to point out that the dry synthetic air had low (please state) concentrations of CO₂, while the filtered outdoor air had atmospheric levels of CO₂. Please list the [CO₂] for all experiments.

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?

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

P. 8027, line 11: At SS 0.20%, Dcrit = 130 nm ($\kappa \sim 0.16$) is more than twice as hygroscopic than Dcrit = 170 nm ($\kappa \sim 0.069$) 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” CaCO₃ with Dcrit = 150 nm at SS = 0.85%, this corresponds to $\kappa \sim 0.0028$. Sullivan et al. (2009b) reported $\kappa = 0.0011 \pm 0.0004$ for CaCO₃.

P. 8027, line 27: The addition of 2-4% NO₃ (as Ca(NO₃)₂, $\kappa = 0.5$ 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% NO₃- detected in the chamber particles can have a significant effect on the particle’s hygroscopicity.

P. 8028, line 24: The authors propose that the Ca(HCO₃)₂ slowly converted to CaCO₃ in the dry CO₂-free chamber. They state this could explain the observed decrease in hygroscopicity which does not become as CCN-inactive as expected for pure CaCO₃. This is only valid if the hygroscopic properties of Ca(HCO₃) and CaCO₃ are differ-

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ent under supersaturated conditions. This would likely require that $\text{Ca}(\text{HCO}_3)_2$ and CaCO_3 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 $\sim 40\%$ of the particle remained $\text{Ca}(\text{HCO}_3)_2$. Does the predicted hygroscopicity of a 40% $\text{Ca}(\text{HCO}_3)_2$ and 60% CaCO_3 particle match the observed hygroscopicity? More quantitative analysis is required here.

P. 8028, line 6: (R1) produces $\text{Ca}(\text{HCO}_3)(\text{aq})$. How would this AQUEOUS reactive alkaline component “protect” the particle bulk from further reaction with $\text{HNO}_3(\text{g})$? It should in fact have the opposite effect; an aqueous layer would allow HNO_3 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_3 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.

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

Sect. 3.6: The interpretation of the chamber experiment observations would be more convincing if an experiment in which NO_x and O_3 was added to the chamber under dry conditions was also performed, to test if the particles are converted to nitrate or not.

P. 8028, line 20: As you know or can estimate the concentration of HNO_3 in the chamber, and know the exposure time, you can compare your observed rate of conversion for the $\text{CaCO}_3/\text{Ca}(\text{HCO}_3)_2$ particles to $\text{Ca}(\text{NO}_3)_2$ with that presented in Sullivan et al. (2009a); how do they compare?

P. 8029, line 2: Please be quantitative instead of saying “a little $\text{Ca}(\text{HCO}_3)_2$ ” and “a significant CaCO_3 fraction”.

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

P. 8029, line 9: The suggestion that the conversion to $\text{Ca}(\text{NO}_3)_2$ facilitates further reaction with HNO_3 because it is more hygroscopic is not strictly correct. It is the higher solubility of $\text{Ca}(\text{NO}_3)_2$ versus CaCO_3 which facilitates further reaction of CaCO_3 with $\text{HNO}_3(\text{g})$, as $\text{Ca}(\text{NO}_3)_2$ will deliquesce $\sim 10\%$ RH. You state that this also explains why $\text{Ca}(\text{NO}_3)_2$ facilitates the reaction while $\text{Ca}(\text{HCO}_3)_2$ does not. Are you assuming that $\text{Ca}(\text{HCO}_3)_2$ is always solid in this discussion?

P. 8029, line 15: Again $\text{Ca}(\text{HCO}_3)_2(\text{aq})$ as a protective layer does not make sense. If you believe $\text{Ca}(\text{HCO}_3)_2$ forms a solid layer under dry conditions that is less reactive than $\text{CaCO}_3(\text{s})$, this must be explicitly stated. (R1) shows $\text{Ca}(\text{HCO}_3)_2(\text{aq})$ as the product, so this is contradictory. Again, the role of carbonic acid must also be considered. 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 the role of differing surface chemistry under wet versus dry conditions, but this is not explained convincingly or clearly here.

P. 8029, line 18: “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.” This sentence does not make sense, please clarify and be specific.

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

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

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?

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Figure 1 is not necessary.

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

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

Fig. 10: The figure caption should indicate when CO₂ was or wasn't present.

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.

Technical Corrections

Abstract, line 16: “believe” should be “belief”.

P. 8017, line 12: “pretends” is not an appropriate word.

P. 8018, line 8: Typo: “the rise RH”.

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.

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

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.

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

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

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