

***Interactive comment on* “Effect of chemical mixing state on the hygroscopicity and cloud nucleation properties of calcium mineral dust particles” by R. C. Sullivan et al.**

R. C. Sullivan et al.

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Included below are the comments from both referees for our manuscript (in italics), followed by our response.

Reply to Referee 1:

General questions to the abstract and introduction: -Mineral dust aerosols are especially important for mixed and ice clouds where they act as ice nuclei (IN) hence these processes should be somewhere mentioned. In addition, is it possible to estimate how important mineral dust aerosol effects are in terms of CCNs versus INs?

We have added a brief discussion of mineral dust as atmospheric IN to the Introduction.

Full Screen / Esc

Printer-friendly Version

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Discussion Paper



We have also briefly discussed what is known about the IN properties of these calcium minerals in the Atmospheric Implications section (see below).

It is not simple to compare the CCN vs. IN ability of mineral dust because both are highly dependent on the dust's mineralogy and atmospheric processing. In general, insoluble aluminosilicate clays are the best IN (Eastwood et al., 2008; Zimmermann et al., 2008), and expected to be the worst CCN due to their insoluble nature.

- About dusts and CCNs - there is a recent study by Lee et al., 2008, ACPD, saying these aerosols can also suppress CCN concentrations which should be mentioned. Could this also be the case for the Ca-dusts?

Lee et al. (2009) discuss the effect of mineral dust that is added to an aerosol population. If the mineral dust particles are not CCN-active under the specific atmospheric conditions then they will simply not contribute to the CCN concentrations, but other CCN-active particles will still be able to serve as CCN. If the mineral dust alters the chemical composition of other particles, by altering gas-particle partitioning for example, or through coagulation, then this can alter the CCN activity of the overall aerosol population. This will indirectly affect the number concentration of CCN-active particles at a certain supersaturation. It is this indirect effect that Lee et al. refer to: "If emissions are predominantly in the coarse mode, CCN(0.2%) decreases in dusty regions up to 10-20% because dust competes for condensable H₂SO₄, reducing the condensational growth of ultrafine mode particles to CCN sizes."

As these processes are physically based the dust chemistry and mineralogy should not have a significant effect. Therefore we would expect the Ca minerals to be able to participate in these physical processes similar to other dust particles. The effect of mineral dust particles on a particle population is a potentially important effect which is distinguished from the effect discussed here, namely the CCN activity of individual dust particles as a function of chemical composition. We now discuss these differences in the Introduction.

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- How important are Ca-dusts on a global scale? Are there other sources except Asia?

Unfortunately there are few global summaries of dust mineralogy available to our knowledge. The most comprehensive summary study is that of Claquin et al. (1999). From their Plate 1, calcite is enriched in the surface soils of most of the deserts in the “dust belt”, comprising between 5-20% of the dust by mass. This includes the northern Saharan and Arabian deserts, the Thar desert in India, and the Gobi and Taklimakan Deserts in Asia. The Kalahari and Namib deserts in southern Africa contain 10-15% calcite, and the Australian deserts are 5-10% calcite. Deserts in Chile and Argentina are composed of 5-25% calcite, while some of the southwestern deserts of North America contain a wide range of calcite, from 0-25% by mass. Therefore, calcite appears to be present to a significant degree of at least 5-10% by mass in the majority of the world’s major dust sources. Furthermore, Asian dust is not particularly enriched in calcite compared to other Asian and African dust regions. The largest calcite-rich dust source is the Kyzyl-Kum desert in central Asia, according to Claquin et al. (1999). Of course this bulk mineralogy does not necessarily represent the composition of the dust particles that are ejected into the atmosphere. Atmospheric dust mineralogy is likely a function of particle size, specific desert source, and can display wide variations between individual particles from the same source (Jeong, 2008).

We have added a brief summary regarding the presence of calcite in global dust sources to the Introduction and Conclusion to emphasize that calcium-containing mineral dust can be emitted from numerous dust regions; it is not restricted to Asian dust alone.

Experimental methods: P5, II.14-18: Statement how the size distributions of dry and wet generated aerosols looked like would be interesting.

The geometric mode of the dry generated particles was typically near 300 nm, while the wet-generated calcium carbonate had a geometric mode near 40 nm. Both displayed only one mode in the SMPS size distributions. We have added these details to the

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manuscript. These are discussed in more detail in our companion manuscript:

Sullivan, R.C., Moore, M.J.K., Petters, M.D., Kreidenweis, S.M., Qafoku, O., Laskin, A., Roberts, G.C., Prather, K.A., Impact of particle generation method on the apparent hygroscopicity of insoluble mineral particles, to be submitted to *Aerosol Science and Technology*.

P7, ll. 2-4: I assume dry dust particles to be rather large, hence doubly charged particles might account for most particles at the lower end of the size distribution. Thus, scans of the critical activation diameter might be only suitable to a limited extend? E.g. for Fig.5, is it possible to data mark points with different symbols according to there scanning technique? Is there a difference between the scans of supersaturation versus scans of the critical activation diameter?

Yes, the large size mode of the dry-generated powders did produce a high fraction of multiply-charged particles in the pseudo-monodisperse aerosol selected by the DMA. This can be directly observed from the activation curves in Figure 4. Both the dry-generated CaCO₃ and CaSO₄ aerosol had a multiply-charged fraction of ~ 0.4 , producing the plateau to the left of the activation diameter in Figure 4. This was accounted for by setting the lower limit of the sigmoidal activation curve equal to the multiply-charged plateau. A multiply charged fraction of 0.4 is in agreement with that calculated based on the measured size distribution of the polydisperse dry powder aerosol, combined with aerosol charging theory. We added some additional explanation about the multiple charging to the text.

The scanning method (size-scans or SS-scans) is indicated in Table 2. While there is some indication that the size-scans produced slightly larger κ values compared to SS-scans for the atomized aerosol, the differences are small, do not appear to be systematic, and are generally within the experimental uncertainties.

Fig. 5: To interpret the data points it would be also useful to have a note which dust was produced wet/dry.

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All wet-generated particles are indicated by open symbols in Figure 5, while all dry-generated particles are shown with filled symbols. This is stated in the figure caption.

Atmospheric Implications: - Is it possible to draw any consequences between the water uptake and INs, e.g. in terms of the freezing mechanism?

Any such conclusions would be highly speculative as a particle's freezing properties are thought to be highly dependent on its hydrophobicity, mineralogy, and surface structure. Thus a particle's water uptake is not the only factor that controls its freezing ability. Since we did not study ice nucleation here we cannot conclude anything definitive regarding these particle's freezing behaviour.

The insoluble minerals could potentially act as deposition or immersion freezing IN. This behaviour is known to be highly dependent on the mineralogy. The few existing measurements of the freezing properties of calcite and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) indicate that they have low freezing potential compared to other minerals (Zimmermann et al., 2008; Eastwood et al., 2008). This information regarding the known IN ability of the minerals studied here has been added to the Atmospheric Implications discussion.

Reply to Referee 2:

General comments: Overall, a very nice paper on CCN activation of mineral dust and processed mineral dust.

Specific Comments: 1. You mention that κ , the hygroscopicity parameter, can deviate from its theoretical, or intrinsic value based on a variety of factors, most of which are related to available soluble mass, either due to particle size, solubility, phase, etc. You quickly mention that surface tension can also play a role. It seems that the hygroscopicity parameter is best suited for inorganic systems where hygroscopicity or solubility plays the key role. It does not strike me as nearly as useful a parameter for organic particles which may have significant surface tension effects. In fact, as you mention, dust may undergo in cloud processing with sea salt and thus may accumulate surfac-

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tants which are a small percentage of the mass, contribute very little to hygroscopicity or soluble mass, but may have a quite profound effect on CCN activation. It seems a bit tortured to fit the treatment of strongly surface active particles under this κ umbrella as you try to do with oxalic acid aged dust. κ is clearly a useful parameter for inorganic systems, but could you comment on the usefulness of κ for strongly surface active systems, especially ones in which the surface active component is a minor component, such as a strong surfactant?

The treatment of organic compounds, including those that are known to lower the air-water interface surface tension, has been discussed in detail in Petters and Kreidenweis (2007). As argued there, organic compounds can be assigned an apparent κ based on a CCN measurement and the assumption of the surface tension of pure water. In this case the apparent kappa serves as a succinct model that simply reproduces the original data. Using this assumption the apparent kappa of the surface active compound can also be used to compute the overall kappa of an internal mixture containing a surface active compound and a non-surface active inorganic compound, without incurring prohibitively large errors. (The example given in Petters and Kreidenweis is humic acid and humic acid internally mixed with ammonium sulfate. Humic acid is one of the strongest surface tension lowering organic compounds known to contribute to the atmospheric aerosol). However, a lower surface tension at the point of activation may occur and the derived apparent kappa does not accurately reflect the water activity part of the theory. Since we expect the apparent kappa for calcium oxalate monohydrate (COH) to be small due to its low solubility, we modified the surface tension term in Eqn. (1) to test if a consistent intrinsic kappa/surface tension pair could be found. It is unclear whether the so-derived surface tension is representative of the actual behavior of the system because surface-to-bulk partitioning of the surfactant (Sorjaama et al., 2004) is not included in this ad-hoc treatment. However, our illustrative calculation is to show 1) that strong surface tension lowering must be assumed to explain the activation behavior of COH, and 2) that this surface tension lowering is at least plausible based on previous literature measurements. Further studies are needed to fully elucidate the

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activation behavior of COH.

2. *You assume an impurity in your insoluble compounds of approximately 1 percent to explain the observed kappa. One could hypothesize that in the case of CaCO₃, this impurity was likely a soluble calcium salt or a soluble carbonate. Regardless, it should be fairly straightforward to attempt to determine possible contaminant using relatively simple analytical techniques. Your single particle mass spectrometer might also have sufficient sensitivity. Was any attempt made to identify contaminants in any of the off-the-shelf compounds used? If not, why? That would seem to strengthen your case for trace impurities being the driver of CCN activation in the cases of insoluble to sparingly soluble salts.*

Actually only 0.1% of a sufficiently soluble, hygroscopic component is required to explain the $\kappa \sim 0.001$ derived for CaCO₃. We have performed a thorough analysis of the potential water soluble contaminants in the calcite powder, using ICP-MS and ion chromatography analysis of the soluble extract of the powder, and single-particle analysis using an aerosol time-of-flight mass spectrometer (ATOFMS) and SEM/EDX microspectroscopy. We found no evidence of soluble contaminants in the dry powder, other than the possibility of other carbonates including sodium and potassium carbonate, as you suggested. We have included a brief summary of these results in the revised manuscript. These results are discussed in detail in a companion manuscript:

Sullivan, R.C., Moore, M.J.K., Petters, M.D., Kreidenweis, S.M., Qafoku, O., Laskin, A., Roberts, G.C., Prather, K.A., Impact of particle generation method on the apparent hygroscopicity of insoluble mineral particles, to be submitted to *Aerosol Science and Technology*.

3. *A minor point, but the calibration of the CCN chamber using ammonium sulfate seems a bit strange. Why not use a more ideal compound that may better approximate a sphere and an ideal solution, something like a highly soluble organic with minimal or known surface tension effects? Ammonium sulfate seems like a very non-ideal calibra-*

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Discussion Paper



tion salt. *If this has been discussed in detail elsewhere in the literature, I apologize.*

Ammonium sulphate is the most commonly used compound for calibration of CCN counters. It is recommended by DMT, the manufacturer of the commercial version of the CCNc based on the same design principles as that used here. Ammonium sulphate is preferred because it has a small shape factor, is stable, non-volatile, sufficiently soluble, and its thermodynamic properties and water activity have been extensively studied. Rose et al. (2008) present a detailed discussion of the calibration of CCN counters using ammonium sulphate aerosol and the associated set of errors from the various effects. Although we agree that a better calibration standard is desirable, we are not aware of a more suitable compound.

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