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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect of surface reaction on the cloud nucleating properties of mineral dust: AMMA aircraft campaign in summer 2006" *by* A. Matsuki et al.

A. Matsuki et al.

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Response to Referee1

We would like to thank the referee for thoroughly reading the article and providing highly relevant remarks. We have addressed each of the referee comments below, and the article is revised accordingly.

General Comments:

This study focuses on cloud processing of dust particles during a special observation period of the African Monsoon Multidisciplinary Analysis campaign. The elemental composition and morphology of dried cloud droplets and clear-sky particles is mea-

sured and used in conjunction with back-trajectory analysis to improve understanding of atmospheric processing of dust. Measurements of the composition of individual dust particles and cloud-droplet residues as a function of altitude are rare, and so data from this study are valuable. The article falls within the scope of ACPD/ACP and would be a decent contribution with some modifications.

A few general concerns:

1. The measurements in this study do not support the detailed discussion of the influence of composition on CCN activity presented in section 4.4. This topic could potentially be addressed by comparing simultaneous measurements of the composition of individual interstitial particles and cloud-droplet residues as a function of particle size and cloud supersaturation. In the current study, however, properties of cloud-droplet residues are compared with average properties of clear-sky particles with little size resolution or information on cloud saturation. Since the composition of clear-sky particles differs in layers above and below the clouds (Fig. 3), the clear-sky particles cannot be considered a reliable reference for the particles in the cloud layer. However, the authors suggest that the influence of composition on CCN activity can be determined from compositional differences of the clear-sky particles and cloud-droplet residues. The weakness of this argument is borne out by the inconclusive nature of their findings (e.g., see paragraphs 1 and 2, p. 1812). Section 4.4 should be condensed to reflect the limited conclusions that can be drawn from the comparison of clear-sky particles with cloud residues. Also, the title of the article should not focus on how surface reactions influence the nucleating properties of dust, since this question cannot be addressed in detail. It would be better for the title to refer more generally to cloud processing of dust particles.

This comment has a very good point, and we have to admit that we could not present enough materials to fully prove our claim that the influence of composition on the CCN activity is responsible for the variations in the dust composition seen in cloud drops. We avoid making any firm assertion and therefore, section 4.4 is condensed in the

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revised manuscript (Figure 7 is also removed). Title of the manuscript is now "Cloud processing of mineral dust: direct comparison of cloud residual and clear sky particles during AMMA aircraft campaign in summer 2006" hence focusing more generally on the cloud processing of dust particles.

2. The authors arguments for the source region of dust being close to the sampling location are unclear and/or unconvincing. For example, I do not understand how vegetation to the south and along the coast of Guinea excludes the possibility of long-range transport of dust to the sampling location (para. 2, p. 1806). Does not the prevalence of dust particles at high altitude suggest that they could have been transported from a long distance? If the dust was not transported a long distance, its prevalence at high altitude might indicate that it was lofted during a convection event close to the source region. However, the authors suggest on p. 1806 (para. 3) that convective events were important only for a limited number of samples. Also, the observations of processed dust particles on p. 1809 (para. 2) in the absence of local industries could indicate that the dust was transport from a long distance. In any case, the authors should present clearer and stronger reasoning for their claim of a local source region.

We are not excluding the possibility of long-range transport nor preceding dust processing. What we tried to express here is that the source of dust particles in the majority of the samples may not be as distant as those suggested by the few peculiar trajectories found in Fig. 4 (b), (c) and (e). The expressions such as 'freshly emitted dust' or 'more close to the sampling location' were employed only in a relative term when compared against those few exceptional samples. Our main focus is to make sure that most of the CVI and clear-sky samples share the typical air mass transport patterns either in the monsoon flux in lower altitudes or easterlies along Sahel belt. We omitted the part describing the locality of the source region since it may have been misleading, and it is very difficult to explicitly locate the source of the dust particles based on the result of the individual particle analysis on airborne dust particles.

3. A few citations to previous work should be clarified: First, an erratum exists for the

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Krueger et al. (2004) paper cited on p. 1800. In the revised Table 1 of the erratum, there is a relatively small percentage of calcium in Saharan dust. A related article by Laskin et al. (JGR, 2005, doi:10.1029/2004JD005206) also reports minimal calcium in Saharan dust. The authors should cite the erratum article for the Krueger et al. (2004) paper. Also, citation of an article that supports the claim of high carbonate content for soil in the proposed source region of this study would be helpful. Second, I think that the particle size range predicted by Kelly et al. (2007) and cited on p.1815 corresponded to a specific supersaturation. That supersaturation should be given along with the particle size range. Third, the Dusek et al. (2006) is not fairly cited on p. 1815, because Dusek et al. (2006) explicitly state (p. 1377 of that article) that composition can dominate size for dust particles.

Indeed, the erratum article of Krueger et al. (2004) shows rather small percentage of calcium in Saharan dust. Their erratum article is also added in the reference list. The work of Claquin et al., (JGR 1999, doi:10.1029/1999JD900416) is cited in the revised manuscript, which can show that both the Saharan and Sahel regions can be potential sources for calcium carbonate particles. Their work indicate higher carbonate content rather in the Saharan regions, but the content is shown in terms of weight percentage in the silt fraction (2μm<Dp<50μm) of the surface soil, and does not exclude Sahel region from being a potential source of carbonate particles in much smaller sizes. The particle size range predicted by Kelly et al. (2007) should correspond to supersaturations in the range 0.1-0.2%. This is given in the revised manuscript. Indeed, the work of Dusek et al. (2006) was not properly cited in the original manuscript. Now their work is cited in relation to the importance of composition on the CCN activity of insoluble particles.

4. In many places, the authors refer to carbonate particles. Particles that had high calcium content and rounded shapes were assumed to be carbonates in this study. While this assumption has some merit, high calcium content would also be associated with particles from soils containing gypsum. The authors should minimize the use of the word carbonates in this article and instead refer to calcium-rich particles or calci-

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umrich particles assumed to be carbonates. This distinction is particularly important in the abstract, because readers may get the incorrect impression that low-Z elements (C,O,N) were measured here.

We believe that our assumption of Ca-rich particles being modified carbonates can be further strengthened by an additional description on the minor S content in most of the Ca-rich particles (added in the part describing the different reactivity of dust particles). Yet, it is true that we have not measured low-Z elements, and therefore we should be more cautious with the use of the word carbonate. We therefore minimized the use of the word in the revised manuscript.

Specific Comments:

p. 1798, line 15 (Abstract): Is sulfate necessarily secondary? Could not sulfate be a primary dust component for soils containing gypsum?

Yes, dust may initially contain sulfate in the form of gypsum and we should not exclude the possible inclusion of S as primary dust component. It is now mentioned in the revised manuscript by adding the following line ' (though fraction of sulfate may be present in the form of gypsum as primary dust component) ' in the abstract. Yet, there were many silicate particles containing excess S/Ca ratio (>1.0) as well as those containing S without Ca, which could not be explained solely by the inclusion of gypsum.

p. 1799, line 23: controversy is probably not the right word here. It is possible that dust could enhance precipitation under some conditions and suppress precipitation under other conditions, and so the situation does not seem controversial.

We avoid using the word 'controversy' in the revised manuscript. Following line is added instead; 'Determining the conditions for which dust particles enhance or suppress precipitation requires further study and understanding of their complex role as CCN.'.

p. 1800, line 4: Is there an article that shows high carbonate content for soil in the

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source region for this study? If so, it would be helpful to specifically identify it here or elsewhere.

The work of Claquin et al. (JGR, 1999) might be useful for showing the geographical distribution of calcite in the surface soils over the African continent. Their work shows higher calcite content rather in the Saharan desert regions than in the Sahel belt (studied area). However, they show calcite content in silt fraction (2<Dp<50μm) in the surface soils and it is not directly comparable with the atmospheric dust having sizes of few microns. At least, their map can give a good idea on the variety of minerals (including calcite) found in the surface soils near the studied area.

p. 1800: It would be useful to say a few words about the purpose of the AMMA campaign in the introduction.

Given the same comment from referee2, an introductory paragraph about the AMMA project was added together with a reference to an overview paper (Redelsperger et al., B. Am. Meteorol. Soc., 87, 1739-1746, 2006).

p. 1801: Please list the specific size ranges of particles and cloud elements that are captured by each inlet and any known uncertainty for these ranges.

Following lines are added in the revised manuscript; "Most recent calibration studies of the CAI inlet in the ECN chamber (Petten, Netherlands), proved that CAI collects particles smaller than 4μm (50% collection efficiency) (L. Gomes, personal communication, 2009)."

"The counterflow of the CVI was constantly adjusted to maintain the diameter of the cloud elements to be 5μm (50% collection efficiency) or larger. Further details on the CVI can be found elsewhere (Schwarzenboeck and Heintzenberg, 2000; Schwarzenboeck et al., 2000)."

p. 1802, lines 4-5: The explanation for particle collection on the impactor stages should be made in terms of Stokes number rather than particle density.

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This explanation is now rewritten in the revised manuscript as, "Practically, supermicron particles are selectively found on the first stage, since the critical Stokes number (corresponds to 50% collection efficiency) would approximately be the same at an aerodynamic diameter of 1.6956;m and Stokes diameter of 1.0956;m with a larger particle density found in the actual atmosphere (e.g. about 2.7g cm-3 for dust particles)."

p. 1802, line 17: Why focus on supermicron particles? Large particles would probably activate regardless of composition. To understand the importance of composition on activation, why not focus on somewhat smaller particles?

Our focus here was to demonstrate on how the cloud processing and CCN activity depend on the mineralogy of the hosting dust particles in the actual atmosphere. We do recognize that larger particles are prone to activate, but we still believe that there is a lack of data from in-situ measurements. We focused on supermicron particles here because dust mineralogy was more diverse and easily distinguished as compared to submicron dust. Submicron dust particles were mostly in flakes of clay-like minerals, and it was difficult to further distinguish the mineralogy solely from elemental composition. Nevertheless, we have also analyzed submicron samples, and the result will be presented elsewhere in relation to their CCN activity.

p. 1802, line 15: What is meant by dry condition? Can you report the RH?

Sample container was kept well below RH<40% by the desiccant.

p. 1803, line 16: Please state the relative humidity associated with the image in Figure 2.

Unfortunately, we have no means to report on the relative humidity inside the vacuum chamber of the transmission electron microscope. Unlike the environmental scanning electron microscopes, we are not actively controlling the water vapor inside the chamber and the images were taken under high vacuum (10^{-5}-10^{-3}Pa). While reaching this range of high vacuum, water for example is expected to be boiling (evaporating) even

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in the room temperature, so we may generally say that we are looking at dried particles under the electron microscopes in high vacuum mode.

p. 1804, line 4: Can you quantify the fraction of cloud residual samples that contained internally mixed sea-salt and dust particles?

Although detected in very few numbers, internally mixed sea salt and dust particles were common among the cloud residual samples (6 out of 7 samples) as indicated in Fig. 3 (light blue color). This is mentioned in the revised manuscript.

p. 1805, lines 11-13: This sentence is a bit confusing. Is the idea that dust aloft was carried from a distance over the Sahel belt, or that dust from the Sahel belt was injected into the air aloft and carried to the sampling locations?

We cannot fully elucidate where and how exactly the dust particles were entrained into the arriving air mass, and both possibilities are mentioned in the revised manuscript. At least we know that dust particles were typically enriched in the air mass arriving aloft, and trajectories suggested that they were brought either by the easterlies along the Sahel belt, or by rather slow air mass circling over Niger and its vicinity (Fig. 4).

p. 1805, line 29: The word interstitial appears to be used incorrectly here, since regions outside of the cloud are being referred to.

Indeed, the word interstitial is not the right word here. Given the suggestion also from referee2, the part "probably due to the interstitial particles" is omitted.

p. 1806, para. 1: If 10% of the total counts were collected outside of the cloud, and interstitial particles are 10% of the in-cloud counts, I am not sure why the condition on cloud operation time is necessary to make this point.

I think it is better to also give the in-cloud operation time (0% in clear-sky and 100% in a homogeneous cloud) in relation to the fraction of clear-sky particles, because this fraction tends to be smaller (<10%) for more homogeneous cloud (in-cloud operation time >50%) naturally due to the shorter period spent in the gaps of the clouds. As for

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the interstitial particles, we do not know their exact contribution in-cloud and 10% of the total counts is rather an overestimation. We made slight changes to the paragraph for better understanding.

p. 1812, lines 2-6: This argument is not convincing. It appears that the influence of composition on CCN efficiency is being determined by comparing differences in cloud residue samples for individual days with the average clear-sky samples over the whole sampling period. I do not think the average clear-sky composition is a reliable reference for the in-cloud particle composition.

Although we might have seen some hint or tendency of the influence of dust composition on CCN efficiency, we have to admit that the comparison of in-cloud and average clear-sky particle compositions alone cannot fully make our points clear. We agree to the referee's comment made at the beginning, that 'this topic could potentially be addressed by comparing simultaneous measurements of the composition of individual interstitial particles and cloud-droplet residues as a function of particle size and cloud supersaturation', and this should rather be taken into account in our future course of study.

p. 1812/1813, 1.-3.: It seems to me that there are additional explanations to the ones listed. For example, maybe silicate particles were larger than the carbonates and activated more readily. Or maybe there were more silicate particles in the air mass where the cloud formed.

Indeed, we have overlooked these additional explanations. It is true that we have to take into account the difference in particles sizes as well as the fraction of particles which remained interstitial, for adequately discussing the relative importance of composition against size on CCN efficiency. Unfortunately though, since we have condensed section 4.4 in the revised manuscript, we are not going so much into details and we no longer list all the possible explanations in the revised manuscript.

p. 1823, Table1: It would be useful to list the number of clear-sky and cloud residue

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counts observed for the categories in the table. Also, group 4 is listed as Calcite and referred to as carbonate throughout the article, but the mineralogy is listed as Calcite or Gypsum in the table. Calcite and gypsum are both present in soils and have very different reactivity. This issue not adequately discussed in the text.

The number of clear-sky and cloud residue counts observed for the categories in Table.1 appears instead in Fig.5. Indeed, gypsum (S/Ca ratio = 1.0) would as well be classified as calcite in the current classification. However, not many pure gypsum particles were found in this study and it would not bias the result significantly. Half of the Ca-rich particles classified as calcite did not even contain S, while only less than 10% reached S/Ca ratio > 0.4. If any, gypsum was only partially present as internal mixtures with the Ca-rich particles. Thus, the good part of the Ca-rich particles was most likely made of calcium-carbonate. A paragraph explaining such minor contribution of gypsum was added in the section describing the difference in reactivity.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1797, 2009.