

***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 Referee2

The authors wish to thank the referee for providing very constructive comments, as well as carefully going through the article to even help improving our English. We have addressed each of the referee comments below, and the article is revised accordingly.

General comments

The paper addresses the question of mineral dust heterogeneous processing with or without clouds within the scope of AMMA, which is in the scope of ACP. New data material is presented from samples collected during an AMMA special observation pe-

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riod. Electron microscopy was used to analyze a significant number of particles. The authors conclude from their data on the processing history of the particles. While the overall conclusions are justified, some details remain challengeable. The used analytic methods are established, but a discussion of measurement uncertainties is missing (though a detailed error discussion would not be in the scope of this publication). A relevant number of related works is properly credited, title and abstract reflect the paper's content. The overall structure is fine, however, some paragraphs found in the results section should be rearranged into the methods section. In general, the use of the language is adequate.

Specific comments

"General specific comment": It is surely not within the scope of this work (and not to be assessed by the methods used), but it should be mentioned (maybe in the introduction), that, of course, also organic materials play a (unknown?) role in the dust-biomass burning-cloud interactions. Their presence might bias the results of the inorganic interpretation.

Thank you for reminding us of the potential role of organic materials on dust particles. It is mentioned rather in the conclusions of the revised manuscript, that this issue should be addressed but remains the future theme due to the technical limitations.

(notation in page number, line(s))

1799, 2-3: Could be more specific, e. g. "The Saharan desert with the Sahelian region is the largest global source".

It is specified so in the revised manuscript.

1799, 11-14: Omit this sentence, as it contradicts the next paragraphs, in which works are listed which were dealing with dust-cloud-interactions.

This part is omitted from the revised version.

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1799, 28: *Dust composition is also dependent on the geological situation, of which the soils derive.*

This is mentioned in the revised version.

1801, 1: *Maybe some introductory remarks should be given on the specifics of the region, where the campaign was performed (why there?) or reference to an AMMA overview paper, if there is any.*

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).

1801, 15: *Insert reference for the CAI inlet*

According to most recent calibration studies of the CAI inlet in the ECN chamber (Petten, Netherlands), first preliminary data analysis of a series of OPC instruments proof that CAI collects at least 4 μm particles (50% collection efficiency) maybe even 5 μm . A detailed data processing is underway (L. Gomes, Personal communication, 2009).

1801, 18: *It is quite unclear at this point, why each cloud element should release (exactly?) one residual particle, though it doesn't seem to have significant impact on the conclusions.*

Ideally, a cloud element entering CVI should release one particle (either an insoluble core, or dehydrating solute, or their internal mixture), but as the referee points out, this may not always be the case in reality even if no cloud breakup takes place in the CVI. The concerned sentence was revised as "The subsequent evaporation of cloud elements in the particle free and dry return flow releases cloud residual particles."

1802, 2: *Surely, the sampling condition was not 1013 hPa: is it a mass flow rate given (which would impact the impactor's cutoff sizes with changing pressure) or a volume flow rate?*

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It is in volume flow rate, and it is specified in the revised manuscript. The cutoff size is not significantly affected because the nozzle of the second impactor stage basically acts as a critical orifice which maintains the constant flow rate.

1802, 26-29: How was the quantification of the elemental concentrations done? By the manufacturer's software (with standards or standard-less), or by a custom model?

It is based on the manufacturer's software with standard-less quantification, and it is specified in the revised manuscript. It is for that specific reason that the low-Z elements (C,O,N) were not accounted for in the quantification.

1803, after 12: Later in the manuscript, a criterion table for particles classification is given. That together with the according text should be incorporated into the methods section here.

The description of the dust particle classification appears in the experimental section of the revised manuscript.

1803, 16-17: change to "Presence of a _silicate_ dust particle..." and exclude the Al content for quartz particles (which is grouped into the silicates later)?

The sentence in question is changed to "Presence of a _silicate_ dust particle...". Actually, almost all particles having atomic fraction $\text{Si} > 85\%$ also contained few % of Al. If quartz particles should not contain Al at all, we will loose the group of particles mostly consisting of Si to compare against the major aluminosilicate particles. Although the mineral classification of the Quartz group members may still be controversial, they are commonly included in tectosilicates, a subclass of the silicate minerals. For these reasons, we classified the Si-dominant particles as quartz to comprise another group of silicates.

1803, 19: Looking on Fig. 1, the particles referred are very rounded, but not exactly spherical in a geometric way, like for instance fly ashes can be (in the limits of measurement error). Maybe this could be misinterpreted, e.g., by people doing optical

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calculations? Would spheroidal (or nearly spherical) be a better expression?

It is true that the rounded particles in Fig. 1 don't show exact spherical shapes. However, the image is only 2-dimensional and we should also consider the height of the particles. From our experience in simultaneously comparing both fly ash and such Ca-rich spherical particles collected in other places, fly ash particles indeed show almost perfect spherical shapes in 3-dimensional sense. With regard to the Ca-rich particles, we often found that they rather had shapes like a flattened disk (Matsuki et al., GRL, 2005). The deliquesced $\text{Ca}(\text{NO}_3)_2$ particle may be present as a solution droplet rather than a crystalline solid particle in the atmosphere, and can be easily deformed (flattened) upon collection by impaction. As evidenced by the single particle levitation experiment by Tang and Fung (J. Chem. Phys. 1997), evaporating $\text{Ca}(\text{NO}_3)_2$ solution droplet maintains its spherical shape even in high vacuum by turning into an amorphous particle containing residual water. Thus, Ca-rich spherical particles are more likely to stay spherical in the atmosphere, and we would prefer to stay with the current expression.

1804, 17-24: Rephrase for better understanding.

This part is rephrased in the revised version as "Although carbonate minerals are reported to comprise significant fraction of the atmospheric irregular dust particles in many parts of the globe (Ganor and Mamane, 1982; Okada and Kai, 1995; Krueger et al., 2004; Kandler et al., 2007), irregularly shaped Ca-rich particles were hardly found in this study. Therefore, the spherical Ca-rich particles containing NO_3^- can be considered as the atmospherically processed carbonate-rich dust particles (i.e. mainly calcite and dolomite)."

1804, 25-27: Does that mean that they are dried droplets? Or are they still liquid or ductile in the electron microscope?

We may generally say that we are looking at dried particles under the electron microscopes in high vacuum mode. These particles seem to retain their spherical outline

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and do not crystallize into irregular forms. At least, we did not witness any rapid desorption or boiling of these particles upon the electron irradiation, which could happen to some liquid or ductile particles.

1805, 8: Insert a reference for the meteorological models or give some properties and limitations, especially with respect to 1806, 20-25 where their validity for convective cases is criticized.

Works by Zeng et al. (Atmos. Environ., 2003) and Doty and Perkey (Monthly Weather Review, 1993) are now in the reference list, describing the METEX model itself as well as model sensitivity on the time interval of wind datasets for an intense and rapidly developing convective system (e.g. MCS).

1805, 16-1806, 8: Integrate this part into the method section; at least the instrumentation should not occur in the results section for the first time.

Following line is now moved to the end of the Aircraft Measurement section; "An optical particle counter (OPC, GRIMM, Portable Aerosol Spectrometer model 1.108) was monitoring the number concentration of larger particles entering the CAI and CVI probes." such that the instrument appears firstly in the method section.

1806, 13-27: The conclusion onto the rather local particles sources seems to be rather weak: You mention model weaknesses for convective events and 28 % of Ca-rich minerals are found, which rather point to the Saharan region, as the Sahelian does not have very high Ca contents in soil (i. e., Claquin et al. 1999, JGR 104, 22243-22256, plate 1).

It is very difficult to explicitly locate the source of the dust particles by comparing the result of the individual particle analysis on airborne dust particles against the soil mineralogy in the potential source regions especially with major elements such as Si and Ca. We have to rely on the trajectory analysis to broadly separate the potential sources (e.g. Saharan dessert, Sahelian region, Arabian Peninsula). With few exceptions, (e.g.

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trajectories b, c, and e in Fig. 4) the 5-day backward trajectories do not stray very far from the Sahelian belt, unless they point back towards the Gulf of Guinea in lower altitudes (in the monsoon flux). Based on this result, we considered the likely dominant source to be of Sahelian rather than Saharan regions. With respect to the Ca contents in the Sahelian soils, the work of Claquin et al. (1999), shows the geographical distribution of calcite content in the soils in terms of weight fraction in the silt size range ($2\mu\text{m} < D_p < 50\mu\text{m}$). Meanwhile, our result is shown in terms of number fraction found in sizes of few micrometers (i.e. clay fraction), so they are not directly comparable. Claquin et al. also point out themselves in their work, soil mineralogy and that of airborne dust particles may not always be directly linked. In my opinion, lower Ca content found in the Sahelian soils as compared to Saharan regions does not exclude the possibility that the Sahelian belt can as well be the source of Ca-rich dust particles in the clay size range ($D_p < 2\mu\text{m}$).

1807, 2-3: How was determined whether particles were of biomass burning origin? What is the possible source of the sulfate particles?

Classification of biomass burning particles was based solely on inorganic elemental composition. Inclusion of potassium-salt in fine particle fraction (not attributable to mineral dust or sea salt) can be used as an indicator of biomass burning origin (e.g. Li et al. 2003, JGR, 108(D13), 8484). It is difficult to locate the exact source of the sulfate particles, but biomass burning can as well be the source of SO_2 in addition to industrial and biogenic emissions.

1807, 7: How many particles were analyzed in total?

In total 1,883 coarse particles were analyzed from the samples collected during the concerned 7 flights. The number is given in the revised version.

1807, 12-19: Move this description to the method section.

The description of the mineral classification is moved to the method section.

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1809, 18: Gypsum is $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.

It is corrected in the revised version.

1809, 22: *Is there a better way to cite this (as "Tobo, personal communication")?*

Their work is now published in GRL and added in the reference list (Geophys. Res. Lett., 36(5), L05817, 2009).

1810, 1-3: *Clear-sky conditions are referencing the time of sampling, but the aerosol particles definitely originate from the soil, so they have already a certain age (probably days). From the given data, we do not know, whether they have been cloud-processed before. Thus, the conclusion of dry uptake of HNO_3 in this case cannot be drawn on base of the given data.*

It is true that we can not exclude the possibility that the particles had been cloud-processed before, although Fig. 6 shows that many dust particles collected in clear-sky conditions were relatively fresh as compared to those collected in-cloud. We avoid making such firm conclusion in the revised manuscript by not excluding the possibility of previous cloud-processing.

1810, 21-23 and Fig. 6: *The figure shows a trend of increasing S+Cl atomic fraction for increasing humidity. Taking into account the uncertainties in quantification of the elemental composition and uncertainties in the relative humidity (we do not know, for fractionated clouds, whether a particle comes from inside or outside a cloud) it is impossible to conclude more from this 25 scattered data points. Everything else is speculative, especially the "excellent" exponential relationship.*

With respect to whether a particle comes from inside or outside a cloud, we have carefully checked the OPC counts during the passage through fractionated clouds (1805, 18-1806, 8 in the original manuscript), and most of the particles collected via CVI can be considered as those came from inside the actual cloud droplets. However, we admit that the CVI samples may still contain few interstitial particles, and given the additional

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uncertainties related to the elemental quantification and relative humidity, we should not be so conclusive if the relationship is really exponential. Instead of showing S+Cl atomic fraction as Y-axis in Fig. 6, we now show the detection frequencies of S and Cl separately. The new figure can nevertheless show that the number of silicate particles containing detectable S or Cl tends to increase with increasing RH, and that the higher numbers are especially found within clouds. We also showed the variation in RH during each sampling in error bars (one standard deviation). The section describing Fig. 6 has been revised accordingly (1810, 9-1811, 16).

1811, 16: What about the nitrate? It should also add to this competition.

Indeed, nitrate should be considered as well. We did not add nitrate in Fig. 6 because nitrate detection by the reaction film is purely qualitative. Even if we employ the detection frequency, unfortunately there will be even fewer data points because not all samples had nitron coatings on. However, knowing that the detection frequency of nitrate on silicate particles was also higher in clouds (e.g. Aluminosilicate I in Fig. 5), a comparable RH dependence might be found for nitrate as well.

1812, 7-1813, 9 and Fig. 7: On which level of significance it can be excluded, that the values of Aug 06/14 are the same as the average, taking into account the standard deviation given in the figure, the (undocumented) uncertainties derived from counting statistics and the errors in elemental quantification? The detailed discussion appears over-interpreted with respect to only two data points while in fact no conclusion can be derived. Although it looks like a lot of work was put into this question, the section should maybe be shortened.

We tried applying 95% confidence intervals for the relative abundances of the different particle groups (Silicate, Ca-rich, Sea salt, others) assuming a multinomial distribution (Höflich et al., J. Environ. Monit., 2005, 7, 419-424) to see if there were meaningful difference in our particle counts. The two cases in Aug 06/14 seemed still having higher number ratio of Ca-rich particles relative to silicates [62.9% (37.2-94.2%) for

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Aug06 and 64.2% (42.9-87.4%) for Aug14] than in average clear-sky samples [31.8% (27.2-36.9%)]. Even so, as the referee points out, these are only two cases and it is undeniable that our discussion was rather over-interpreting. Therefore, section 4.4 is now shortened to reflect the limited conclusions that can be drawn from the data we have. Figure 7 is also removed.

1815, 27-1816,8: The work of Dusek et al. is not well comparable to this work, so there is not really a contradiction. Dusek et al. investigated the total number population of aerosol and, thus, concentrated on the submicron fraction close to the CCN activation border (see also the size distribution plots in their work). In the submicron regime, the particle size is indeed the main (though not the only, as Dusek et al. also state) controlling factor (which we should have suspected since Köhler). In contrast, this present work focuses on details of the supermicron particles, where chemistry obviously plays a role. However, in the present work it is not quantified, how many of the mineral dust particles remain interstitial between the cloud droplets. So we do not know whether the influence of chemistry on activation is important for a large number fraction of the supermicron particles. The argumentation around the supersaturation is vague ("it is said").

We admit that the work of Dusek et al. (2006) was not properly cited and we should avoid using the expression 'contradiction'. Our intention here was rather not to rule out the regime where chemistry may also play an important role, especially when insoluble particles such as mineral dust are concerned. Given the weakness of not presenting precise information on the supersaturation and how many of the mineral dust particles remained interstitial, we should avoid making any strong assertion in section 4.4 but rather state that this issue remains unsolved.

1823: If "gypsum" really was classified as "calcite", shouldn't this have a significant bias on the result interpretation, as calcite probably is at the beginning of a processing chain, and gypsum rather at the end? How frequent was gypsum observed? Are there minimum Al and Si concentrations for a particle to be sorted into group 2 or 3?

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Indeed, gypsum (S/Ca ratio = 1.0) would as well be classified as calcite in the current classification. However, not many 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 calcite. Most of the calcite particles more or less contained fractions of Al and Si, suggesting that they were internally mixed with aluminosilicate minerals, so we chose Si/Ca < 0.5 to distinguish calcite dominant particles from the aluminosilicate dominant particles.

Technical corrections and phrasing suggestions

Thank you very much for the thoughtful corrections and suggestions for improving our English. Each of the following corrections is made in the revised manuscript.

1798, 2-9: Shorten sentences.

This part is shortened in the revised manuscript as; "In order to gain insights into the characteristics of the mineral dust particles incorporated in the actual cloud droplets and the related cloud processing, the French ATR-42 research aircraft equipped both with a counterflow virtual impactor (CVI) and community aerosol inlet was deployed in Niamey, Niger (13°30' N, 02°05' E) in August 2006 within the frame of the African Monsoon Multidisciplinary Analysis (AMMA) project."

1798, 10: Omit "Both" and "later" Done.

1798, 11: "using a transmission" and "and a scanning" Done.

1798, 12: "with an energy" and "spectroscopy" Done.

1798, 20: "A surprisingly" Done.

1798, 22: "hygroscopicity, resulting from their reaction" Done.

1798, 24: "there are sufficient" Done.

1800, 12: *change "Implication" to "A result" Done.*

1800, 16: *"point of their emission" Done.*

1800, 24-28: *Shorten Done.*

1801, 7-8: *Omit "In order to ... acting as CCN" Done.*

1802, 15: *"flight, the particle-laden" Done.*

1802, 20-22: *"About 10 randomly chosen fields of view per sample were imaged at a constant magnification (3000x) at 120 kV acceleration voltage." Done.*

1803, 2-3: *"and low atmospheric" Done.*

1803, 3-5: *"Samples failing to have more than 30 analyzed particles (6 out of 37) were excluded from this work due to the lack of representativeness." Done.*

1803, 8-9: *"..., half of the sample substrates were prepared using the above-mentioned grids with additional nitron (C₂₀H₁₆N₄) coating." Done.*

1803, 21: *Omit "Other" Done.*

1804, 1: *"and different clay minerals" Done.*

1804, 6: *Omit "found in this study often" Done.*

1804, 9: *"collodion film showed a spherical/spheroidal" Done.*

1804, 11-13: *"At least 60 % up to 90 % of the Ca-dominated particles on the reactive nitron reagent film contained NO₃-. It becomes evident ... " Done.*

1804, 18: *"of the atmospheric irregular dust particles" Done.*

1804, 18-24: *reword*

This part is reworded as; "Although carbonate minerals are reported to comprise significant fraction of the atmospheric irregular dust particles in many parts of the globe

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(Ganor and Mamane, 1982; Okada and Kai, 1995; Krueger et al., 2004; Kandler et al., 2007), irregularly shaped Ca-rich particles were hardly found. Therefore, the spherical Ca-rich particles containing NO_3^- can be considered as the atmospherically processed carbonate-rich dust particles (i.e. mainly calcite and dolomite)."

1805, 29: *Omit "probably due to the interstitial particles"* Done.

1806, 1: *"counted in the gaps of the cloud"* Done.

1807, 7: *"1495 of the total supermicron particles (nnnn) were ..."* Done.

1807, 15-16: *"Particles enriched in Ca were termed Calcite (CaCO_3) and those enriched in Ca and Mg Dolomit ($\text{CaMg}(\text{CO}_3)_2$)."* (as it is found in the table) Done.

1808, 15-16: *Omit "as geologists ... silicates)." Done.*

1809, 1: *"roll" 8211;> "role"* Done.

1809, 10-11: *"Cl/Na ratio is"* Done.

1809, 21: *"The possibility"* Done.

1813, 24: *"pathway (3.) may"* Done.

1829: *"Characters (a) to (e) show averages for the peculiar air-mass trajectories identified in Fig. 4" (?)*

This part appears in the revised manuscript as; "Characters (a) to (e) show detection frequencies for the samples associated with the peculiar air-mass trajectories identified in Fig. 4"

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

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