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**Effect of surface  
reaction on CCN  
properties of mineral  
dust**

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# Effect of surface reaction on the cloud nucleating properties of mineral dust: AMMA aircraft campaign in summer 2006

A. Matsuki<sup>1,3</sup>, A. Schwarzenboeck<sup>1</sup>, H. Venzac<sup>1</sup>, P. Laj<sup>1</sup>, S. Crumeyrolle<sup>2</sup>, and L. Gomes<sup>2</sup>

<sup>1</sup>Laboratoire de Météorologie Physique, Université Blaise Pascal, Clermont-Ferrand, France

<sup>2</sup>Centre National de Recherches Météorologiques, Météo-France, Toulouse, France

<sup>3</sup>Frontier Science Organization, Kanazawa University, Japan

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Correspondence to: A. Matsuki (matsuki@staff.kanazawa-u.ac.jp)

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## Abstract

In order to gain insights into the characteristics of the mineral dust fraction which actually serves as cloud condensation nuclei (CCN) including the related cloud processing, this study proceeded to directly collect CCN and compare their mixing states with that of the clear-sky aerosol particles. To pursue this goal, 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°30' E) in August 2006 during one of the special observation periods (SOP) of the African Monsoon Multidisciplinary Analysis (AMMA) project.

Both cloud residual and clear-sky particles were collected separately and later analyzed individually using transmission electron microscope (TEM) and scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDX). The analysis revealed interesting characteristics on the coarse dust particles ( $D_p > 1 \mu\text{m}$ ), particularly those which likely had acted as CCN.

Traces of heterogeneously formed secondary sulfate, chloride and nitrate were found on many dust particles. These secondary species were particularly enhanced in clouds (i.e. cloud processing). The study illustrates that carbonates (Calcite, Dolomite) contained the secondary species in significantly larger frequency and amount than the silicates (Quartz, Feldspar, Mica, Clay), confirming that carbonates represent the most reactive fraction of the mineral dust. Surprisingly large fraction of the carbonate particles were already found in deliquesced form even in clear-sky conditions, most probably reflecting their extreme hygroscopicity following the reaction with  $\text{HNO}_3$  gas. There were also some indications that the large carbonate particles may be acting primarily as CCN under very low supersaturations, unless there is sufficient hygroscopic coatings on the silicates particles.

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## 1 Introduction

Mineral dust emitted into the atmosphere by the surfaces of the continental arid and semi-arid regions comprises an important fraction of the atmospheric aerosol. The African continent is by far one of its largest global sources (Tanaka et al., 2005). During the course of its aerial long-range transport, dust particles may influence the climate by interfering directly with the atmospheric radiative processes (Sokolik et al., 2001; Haywood et al., 2003) and indirectly by modifying the distribution of clouds (Lohmann et al., 2004).

The important role of dust particles acting effectively as ice nuclei (IN) has been rather well recognized (Isono et al., 1959; Heintzenberg et al., 1996; DeMott et al., 2003; Sassen et al., 2003; Twohy and Poellot, 2005). On the other hand, their potential for serving as cloud condensation nuclei (CCN) has been significantly overlooked probably due to the generally well accepted assumption that these particles are mostly water insoluble silicates (Baltensperger and Nyeki, 1997).

Dust particles may induce diverse indirect effects also through their interaction with warm clouds. On the one hand, they are suggested to serve as “giant CCN” which would facilitate the formation and growth of large cloud droplets into precipitating sizes (Levin et al., 1996; Feingold et al., 1999). On the other hand, dust particles are also claimed to suppress precipitation by causing the water competition among the increased number of CCN (Rosenfeld et al., 2001), known as cloud albedo and cloud lifetime effects (Twomey, 1974; Albrecht, 1989). Lack of measurements and understanding of the conditions for which dust particles can serve as CCN may be the cause of the controversy. The CCN activity of dust particles may depend highly on many environmental factors, such as the supersaturation and aerosol size distribution. Of particular concern is the influence of complex dust mineralogy and the following atmospheric processing, which will be the main focus of this study.

The mineral composition of individual dust particles is quite diverse already at the initial entrainment into the atmosphere. It is dependent on the soil type in the source

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regions. Although silicates are the largest component of the earth's crust, surface soils in some regions are reported to have significantly high contributions of carbonates and other evaporites (Ganor and Mamane, 1982; Okada and Kai, 1995; Formenti et al., 2003; Krueger et al., 2004; Kandler et al., 2007).

5 The atmospheric processing of dust particles further complicates the issue. During transport in the troposphere, dust particles provide reaction surface for acidic gases such as SO<sub>2</sub> to form sulfite, which is subsequently oxidized to sulfate, for example by gaseous ozone (Usher et al., 2002; Trochkin et al., 2003). Presence of nitrate can be found on the dust particles due to the heterogeneous reaction with HNO<sub>3</sub> and other  
10 nitrogen oxides (Wu and Okada, 1994; Sullivan et al., 2007a). Mineral surface is also reported to act as a sink for the HCl gas liberated from sea salt particles (Zhang and Iwasaka, 2001; Ooki and Uematsu, 2005; Sullivan et al., 2007b). Implication from these processes is the enhanced hygroscopicity of dust particles. In turn, such soluble coatings on aluminosilicate particles may have detrimental effect on their innate ice  
15 forming ability (Archuleta et al., 2005). Therefore, the cloud nucleating properties of dust particles at the initial point of its emission may be significantly altered after the long-range transport. The accumulation of secondary acids may have other climatic implications apart from potentially altering the ability of the dust particles serving as CCN or IN. For example, marine productivity in the remote oceans may be enhanced  
20 as a result of the increased iron solubility (Zhu et al., 1992).

Many of the previous works were based mainly on the analysis of aerosols under cloud-free conditions. They provided valuable information regarding the extent of dust modification in the atmosphere. However, it was often difficult to prove whether or not the observed modification involved any preceding cloud processing. In order to characterize the supposed dust fraction which serves effectively as CCN, and to directly  
25 compare the cloud processed particles against those remained cloud-free, it is desirable to collect not only the aerosol particles, but also particles incorporated in the actual droplets, and to compare their mixing states through individual particle analysis.

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## 2 Aircraft measurement

The frequent development of Mesoscale Convective Systems (MCS) and their easterly propagation are notably the main feature of the monsoonal season over the area studied during the AMMA project. However, it is not realistic to direct a manned aircraft into these highly convective systems. Instead, shallow stratocumulus clouds were studied under relatively calm conditions.

In order to answer the above questions about the potential of mineral dust particles acting as CCN, the French ATR-42 research aircraft was deployed near Niamey, Niger (13°30' N, 02°30' E) in West Africa, during one of the special observation periods (SOP2a2: 2–19 August 2006) of the African Monsoon Multidisciplinary Analysis (AMMA) project. The ATR-42 was equipped with two separate inlet probes, namely, the community aerosol inlet (CAI) and the counterflow virtual impactor (CVI). The CAI is a forward facing aerosol inlet developed by Centre National de Recherches Météorologiques (CNRM, France), which is designed for the ATR to allow isokinetic and isoaxial sampling relative to the incoming air stream. The CVI (Ogren et al., 1985) is designed to exclusively collecting cloud elements (cloud droplets and ice crystals), while rejecting interstitial aerosol particles. Evaporation of cloud elements injected in the particle free and dry return flow releases one residual particle per cloud element. Further details on the CVI can be found elsewhere (Schwarzenboeck and Heintzenberg, 2000; Schwarzenboeck et al., 2000). Thus, switching between the CVI in cloud and CAI in clear-sky conditions allowed direct sampling of either the cloud residual or total aerosol particles.

## 3 Sampling and analysis

Particles entering the two probes were directly collected using two-stage cascade impactors. The impactor used in this study is basically identical to that described in Matsuki et al. (2005a, b). The aerodynamic diameter at which particles are collected

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with 50% collection efficiency was at  $1.6\ \mu\text{m}$  and  $0.2\ \mu\text{m}$ , respectively, at the first and second stage of the impactor with a flow rate of approximately  $1.0\ \text{L}\ \text{min}^{-3}$  ( $1013\ \text{hPa}$ ,  $293\ \text{K}$ ). Practically, supermicron particles are selectively found on the first stage due to the larger particle density found in the actual atmosphere (e.g. about  $2.7\ \text{g}\ \text{cm}^{-3}$  for dust particles), while those on the second stage are representative of the accumulation mode ( $0.1 < D_p < 1\ \mu\text{m}$ ) particles.

One representative flight track of the ATR-42 aircraft is shown in Fig. 1. In every flight, 5 or 6 samples were collected corresponding to the number of stacked horizontal flight legs made during the stepwise descent from 5 km down to 0.4 km (above mean sea level), which included 1 or 2 samples via CVI in the presence of stratocumulus clouds. In total 7 flights of that type were conducted in the vicinity of Niamey on 4, 5, 6, 7, 13, 14 and 17 August 2006. Each sampling lasted 15–20 min depending on the duration of the respective flight leg. Collodion film on an electron microscopic grid made of nickel (MAXTAFORM H7 400 mesh) was chosen as the sampling substrate. After the flight, particle laden grids were kept sealed under dry condition until they were analyzed in the laboratory on individual particle basis.

The current study is based mainly on the morphological and chemical analysis of individual supermicron particles found on the first stage of the impactor. The samples were imaged firstly under a digitized transmission electron microscope (TEM, Hitachi H-7650) to obtain high resolution images of the particles. About 10 fields of view with constant magnification (at  $\times 3000$ ) were imaged randomly over a sample at 120 kV acceleration voltage. Then, the same fields were located again under a scanning electron microscope (SEM, JEOL, JSM-5910LV) coupled to an energy dispersive X-ray spectroscopy (EDX, Princeton Gamma-Tech, Prism2000), in order to obtain the elemental composition of the individual supermicron particles. The X-ray spectra were collected at 20 kV acceleration voltage and 15 mm working distance. The relative atomic fractions (%) of all the detected elements (except lighter elements such as C, N and O) were quantified based on the X-ray spectra (i.e. a pure  $\text{CaSO}_4$  particle would give atomic fractions of 50% Ca and 50% S).

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On average, 50 particles on each grid were analyzed on manual basis. Some sam-  
ples had insufficient particle loadings mainly due to the short collection time and small  
atmospheric concentrations. Such samples failing to have more than 30 analyzed par-  
ticles (6 out of total 37 samples) were excluded from the current result and discussion  
5 due to the lack of representativeness in terms of the relative abundance of various  
particle types and respective average composition.

Due to the technical difficulty related to the detection of lighter elements such as  
Nitrogen by the EDX analysis, samples were made alternately using the above men-  
tioned grids and those with additional nitron ( $C_{20}H_{16}N_4$ ) coating. The nitron reagent  
10 film is a reactive film for identifying particulate nitrate (Isawa and Ono, 1979). After  
sampling, nitron film is treated in the octanol vapor in order to facilitate precipitation of  
needle like crystals specifically around the particles containing nitrate ( $NO_3^-$ ).

## 4 Results and Discussion

### 4.1 Major particle types and their origin

15 A representative electron micrograph of cloud residual particles collected via CVI is  
shown in Fig. 2. Presence of a dust particle can be identified by the typical irregular  
shape and the dominant X-ray peaks corresponding to Al and Si (Fig. 2a). More than  
90% of such coarse particles exceeding  $1\ \mu\text{m}$  in diameter composed of the following  
3 major types, namely, silicate dust particle (Fig. 2a), sea salt (Fig. 2b), and spherical  
20 particles enriched in Ca (Fig. 2c). These three types were dominating regardless of  
whether they were cloud residual (in-cloud) or clear-sky particles. Other minor types  
included particles rich in Cl and K that are linked to biomass burning (Mouri et al., 1996;  
Li et al., 2003). Few particles were found enriched in P and K, which may be attributed  
to biogenic origin (Artaxo et al., 2002).

25 Silicate particles contained elements such as Na, Mg, Al, Si, K, Ca, Ti and Fe, in  
various combinations, indicating that they are composed of (or mixtures of) quartz,

feldspar, mica, amphibole and other clay minerals. Most of the sea salt particles collected in the vicinity of Niamey had lower Cl/Na atomic fractions relative to sea water, which is an indication of aging due to the Cl liberation during transport (Hara et al., 2002). Sea salt particles internally mixed with silicates were scarce even amongst the cloud residual samples.

A majority of the Ca-rich particles found in this study often included fractions of Al and Si which implies their crustal origin. However, their spherical shape does not match with the generally accepted concept of the “irregular” dust particles. About 90% of the total Ca dominant particles found on the inert collodion film gave the spherical shape (Fig. 2c), and they were not as electron dense as the irregular silicate particle (Fig. 2a).

With respect to the Ca dominant particles collected on the reactive nitron reagent film, at least 60% or even up to 90% of them were found to contain  $\text{NO}_3^-$ . It is becoming evident that mineral dust particles enriched in carbonate minerals such as calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{MgCa}(\text{CO}_3)_2$ ) react with  $\text{HNO}_3$  gas to form extremely hygroscopic  $\text{Ca}(\text{NO}_3)_2$  or  $\text{Mg}(\text{NO}_3)_2$  which are suggested to readily deliquesce under subsaturated atmospheric conditions (Krueger et al., 2003, 2004; Laskin et al., 2005; Matsuki et al., 2005b). Carbonate minerals are reported to comprise significant fraction of the atmospheric dust particles in many parts of the globe (Ganor and Mamane, 1982; Okada and Kai, 1995; Krueger et al., 2004; Kandler et al., 2007). In this study however, irregularly shaped carbonate particles were hardly found. Instead, they were almost entirely silicate particles. The absence of irregularly shaped carbonate particles is most probably due to the replacement by the spherical Ca-rich particles containing  $\text{NO}_3^-$ . Thus, we concluded here that the observed spherical particles were indeed the processed carbonate rich fraction of the dust particles (i.e. mainly calcite and dolomite).

The spherical shape of carbonate particles most likely results from the expected amorphous metastable state of  $\text{Ca}(\text{NO}_3)_2$  that contains residual water persisting even in high vacuum (Tang and Fung, 1997). From the bulk volume of the semi transparent particle, Ca, S and/or Cl are commonly found for elements  $Z > \text{Na}$  (Fig. 2c). The X-ray signals of Al and Si in the Ca-rich particles were relatively strong in the bright spots

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(dark spots under TEM) often found in the particle centers. These spots are most likely the aluminosilicate residues suspended in the amorphous  $\text{Ca}(\text{NO}_3)_2$ .

If we compare the relative abundance amongst the mentioned particle types, there was a tendency that sea salt particles predominate in the lowest 1.5 km (Fig. 3). In the contrary, dust particles (Sum of silicate and Ca-rich particles: Quartz+Aluminosilicate+Calcite+Dolomite) predominated over sea salt in higher altitudes (>1.5 km). The 5-day backward trajectory analysis clearly depicts the complete turnover of the wind regime across this altitude (Fig. 4). The trajectory calculation was made using METEX developed by NIES-CGER. Figure 4 shows that the air mass arriving at lowest 1.5 km came from the gulf of Guinea due to the prominent south-westerly monsoon flux typical of the season. In higher altitudes (>1.5 km), the air mass approached rather from the east, due to the presence of the African Easterly Jet (AEJ), thus carried dust particles along the semi-arid regions of the Sahel belt. At even higher altitudes (4–5 km), air mass often arrived after making a descending anticyclonic curve around the Saharan high (Cook, 1999).

Interestingly, dust particles were more abundant than sea salt particles even in all the cloud residual samples for the above mentioned 7 local flights in the vicinity of Niamey (Niger). With respect to the cloud residual sampling by CVI however, one has to evaluate the degree of possible contamination by the large and heavy interstitial particles. Due to its large size and density, dust particles have the potential to aerodynamically mimic the cloud droplets. An optical particle counter (OPC, GRIMM, Portable Aerosol Spectrometer model 1.108) was monitoring the number concentration of larger particles entering the CVI probe. In reality, clouds are spatially inhomogeneous and the observed stratocumulus clouds were quite often patchy. Consequently, the number concentration of cloud residual particles during a given CVI operation fluctuated remarkably as the aircraft repeatedly entered and left the cloud patches. Ideally, the count should drop to 0 when the aircraft leaves the cloud. Although significant counts appeared only when the aircraft was inside the cloud, few counts continued to appear even outside of the cloud patches, probably due to the interstitial particles. The sum of

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particles  $D_p > 1 \mu\text{m}$  counted in the holes of the cloud was up to 10% of the total counts obtained during a given CVI operation. Even if we assume that a similar percentage of interstitial particles was collected by the CVI inside the clouds (meaning that largest particles would not at all have been activated), the sum of collected interstitial particles within clouds plus total particles outside cloud could have been up to 20% on a CVI sample leg, for in cloud operation times of at least 50%. Therefore, most of the coarse particles (at least 80%) collected via CVI can be considered as those found in the actual cloud droplets.

Since the stratocumulus clouds often appeared close to the boundary of the two wind regimes at about 1.5 km, the air mass trajectories arriving at the level of CVI operations showed the mixed characteristics of both the monsoon flux and the easterlies along the Sahel belt (Fig. 4). The vegetation cover increases dramatically towards the south and it is deeply forested along the coastline facing the gulf of Guinea. Hence it is suggested that the majority of the dust particles collected via CVI in the current study are more likely to be freshly emitted dust particles incorporated more close to the sampling location along the Sahelian semi-arid region, rather than those arriving after the long-range transport (e.g. from Saharan desert).

In order to make a strict comparison between the mineral composition found in and outside of clouds, several clear-sky sample with peculiar trajectories which differ significantly from those of the CVI samples are extracted and marked by alphabets (Figs. 3 and 4). For example, trajectories (b), (c) and (e) suggest that the collected dust particles arrived after long-range transport from even distant sources (e.g. Saharan desert). The rapid ascending motion in trajectories (a) and (d) suggest presence of exceptionally strong convection (e.g. MCS) which significantly undermines the relevance of the model output. Therefore, dust particles found within samples (a) to (e) may have different sources, or previously undergone intense atmospheric processing (longer lifetime, cloud processing in highly convective clouds, etc.).

Though it will be discussed more in detail in a companion paper, dust particles found in the accumulation mode ( $0.1 < D_p < 1 \mu\text{m}$ ) were almost entirely hexagonally shaped

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particles enriched in Al and Si (most likely to be kaolinite). They accounted for roughly 20% of the analyzed submicron particles. Majority of the particles were biomass burning (50%) and sulfate particles (30%). Only few sea salt particles were found. In general, the submicron particles in higher altitudes tended to show signs of aging with increasing contribution from sulfates.

## 4.2 Heterogeneous reaction on dust particles

Out of the total supermicron particles analyzed in all samples, 1495 particles were identified as mineral dust, including the modified carbonates (i.e. Calcite and Dolomite). They were further segregated into 5 mineral groups depending on the relative atomic fractions found in every particle. For example, “Quartz” ( $\text{SiO}_2$ ) was the group of particles having more than 85% of Si. The largest number of the dust particles was assigned to “Aluminosilicate I” such as Feldspar, Mica and various clay minerals. They are more difficult to distinguish solely from the elemental composition, however, particles resembling Amphibole, or particles with exceptionally high Fe content, as well as Ti containing particles were extracted to form another group “Aluminosilicate II”. Particles enriched in Ca and Mg were termed Calcite ( $\text{CaCO}_3$ ), and Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ). As mentioned earlier, particles falling into such carbonate groups were predominantly the Ca-rich spherical particles. The classification criteria used for the grouping of mineral dust particles are summarized in Table 1.

The X-ray spectra (including the samples with nitron reagent film) showed that the significant fraction of dust particles contained S, Cl, and  $\text{NO}_3^-$ . Figure 5 compares the detection frequencies of S, Cl, and  $\text{NO}_3^-$  among the dust particles of different mineralogy. Clearly, the detection frequencies of S, Cl, and  $\text{NO}_3^-$  were unevenly distributed in the 5 mineral groups. Such mineralogical dependence should not be seen if these components became internally mixed with the dust particles as a result of coagulation (Matsuki et al., 2005a). Further, the overall picture did not change even if we excluded all dust particles containing Na, demonstrating the minor effect of the possible mixing

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of sea salt and dust particles. Thus, Fig. 5 demonstrates the selective formation of sulfate, nitrate, chloride upon the heterogeneous uptake (and subsequent oxidation) of reactive gases (e.g.  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{NO}_x$ ,  $\text{HCl}$ ,  $\text{O}_3$ ) on the different mineral surfaces (Goodman et al., 2001; Hanish and Crowley, 2001; Underwood et al., 2001; Usher et al., 2002, 2003; Ooki and Uematsu, 2005; Vlasenko et al., 2006).

It was also found that, S, Cl, and  $\text{NO}_3^-$  had a common distribution pattern in the 5 mineral groups (Fig. 5). Quartz particles were the least reactive of all groups (<10%). Aluminosilicate II group was separated from the majority of the clay minerals (Aluminosilicate I), in order to isolate the possible uptake enhancement by the catalytic behavior of transition metal oxides such as Fe and Ti (Brandt and Vaneldik, 1995; Ivanov et al., 1998). However, the detection frequencies for Aluminosilicate II were found to be similar in extent, or only slightly higher (16–23%) than Aluminosilicate I (10–17%). In contrast, Calcite and Dolomite showed exceptionally higher detection frequencies in all the three components (42–73%). It is well known that these two major carbonates are particularly susceptible to acids, as geologists often use HCl solution to conduct a quick test to detect carbonate presence in the rocks (most of which consist of silicates). Figure 5 demonstrates that this alkaline nature of the carbonates is also reflected in the high uptake coefficient of the acidic gases.

### 4.3 Cloud processing of dust particles

One of the main interests of the current study is to demonstrate how such processing of dust particles would further proceed in the actual cloud droplets (i.e. cloud processing). Figure 5 also compares the detection frequencies of S, Cl, and  $\text{NO}_3^-$  between the dust particles collected via CVI (in-cloud) and CAI (clear-sky). If we focus firstly on the major Aluminosilicate I group represented by the largest number of analyzed particles (845 particles out of total 1495), it is evident that the detection frequencies of all the three components showed remarkable increase of about two to three-fold in-cloud (32–41%) as compared to clear-sky conditions (10–17%). This is most likely reflecting the accelerated uptake and oxidation of the acidic gases in the aqueous phase, although

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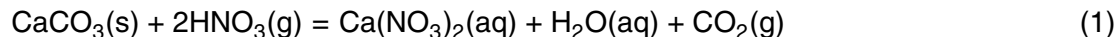
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incorporation of interstitial aerosols into the cloud droplets may also play a roll in mixing these components with dust particles. For the Calcite group represented by the second largest number of particles (479 particles), the increase in the detection frequency of S was not as evident as for Cl and  $\text{NO}_3^-$ . It was suggested that the rate of S accumulation onto carbonate particles was not particularly higher in-cloud as compared to clear-sky conditions, at least under the situations encountered during the current campaign.

It was surprising to find almost all carbonate particles in the modified unusual spherical form (Fig. 5) despite considering the proximity to the dust source region and the remoteness from heavily inhabited cities or major industries. Unfortunately, gaseous data is not available on the same aircraft. At least, the observed deficit in the Cl/Na is a sign that gaseous HCl had been released from the sea salt particles. Also, local biogenic emission of  $\text{NO}_x$  from wetted soils in the Sahel has been spotted by the British BAe-146 aircraft deployed during the same campaign (Stewart et al., 2008).  $\text{O}_3$  formation was also observed in relation to this  $\text{NO}_x$  emission from soils.

It is generally expected that chloride and nitrate are more prone to concentrate on supermicron dust particles, unless particles had previously taken up exceeding amount of non-volatile sulfate (Sullivan et al., 2007). The hygroscopicity of the resulting Ca salts may depend highly on the reacting acidic gas. If gypsum ( $\text{CaSO}_4 \times \text{H}_2\text{O}$ ) forms as a result of  $\text{SO}_2$  uptake and subsequent oxidation on a calcite particle, the change in the hygroscopicity may not be as dramatic as in the case of  $\text{Ca}(\text{NO}_3)_2$  formation, since gypsum is only slightly soluble (Kelly et al., 2007). Possibility remains that  $\text{CaCl}_2$  also turns calcite particles very hygroscopic (Tobo, personal communication, 2009). It is also interesting to find the formation of water along the  $\text{CO}_2$  emission during the effervescence as shown in Eq. (1).



Hence, the acquisition of hygroscopicity and water molecule is a combined process. Further uptake of the acidic gas and water vapor in the atmosphere can lead to the eventual dissolution of an entire carbonate particle, which explains the presence of the observed Ca-rich spherical particles with high  $\text{NO}_3^-$  detection frequency (Fig. 5).

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The fact that almost all calcite particles were in their characteristic spherical form even in clear-sky conditions suggests that the carbonates do not necessarily need to experience cloud for the formation of such spherical particles. It indicates that the active uptake of  $\text{HNO}_3$  gas on the carbonate particles and the consecutive deliquescence readily takes place even under relatively dry conditions in the actual atmosphere, as suggested by the laboratory experiments and modeling studies (Tang and Fung, 1997; Krueger et al., 2003, 2004; Kelly and Wexler, 2005; Laskin et al., 2005; Gibson et al., 2006a, b).

In order to take a closer look on the effect of supposed adsorption of water molecules on the silicate surface and the eventual immersion into the droplet, the sum of average atomic fractions of S and Cl found in all silicate particles (Quartz+Aluminosilicate I and II) were plotted as a function of mean relative humidity at which the particles were collected (Fig. 6). While the detection frequency shown in Fig. 5 is strictly qualitative, the relative atomic fraction calculated based on the X-ray spectra can provide semi-quantitative information on the elemental composition. Unfortunately however, N element was not quantified due to the low sensitivity of the EDX detector, and nitron reagent film remains purely qualitative. As for the CVI samples, the mean relative humidity was obtained simply by averaging over the entire CVI operation regardless of how patchy the cloud layer was, hence CVI samples collected in more broken clouds tended to give smaller relative humidity <100%.

An excellent relation was found in Fig. 6, such that the amount of S and Cl in the silicate particles increases exponentially with increasing relative humidity, and that the highest values were found especially among the particles collected in clouds. Similar acceleration of  $\text{SO}_2$  uptake as a function of relative humidity has been reported previously (Huray et al., 1978; Dlugi et al., 1981; Matsuki et al., 2005a), however, Fig. 6 steps further to isolate the actual cloud processing from the clear-sky processing. Since CCN particles may undergo on average ten evaporation/condensation cycles before they finally precipitate (Pruppacher and Jaenicke, 1995), this is a clear demonstration that the dust particle composition can be significantly altered depending on the

cloud presence along their long-range transport.

Another interesting feature is that, the samples related to the peculiar air-mass trajectories (trajectories a to e in Fig. 4) stray significantly away from the majority of the plots in Fig. 6. The trajectories suggested that dust particles in these samples may either have experienced very long-range transport, or encountered highly convective situations and thus, significant cloud processing. This is well reflected in the amount of S+Cl found in silicate particles such that they do not generally fit with the exponential trend seen in Fig. 6. In the contrary, majority of the samples may have incorporated dust particles in the Sahelian belt in the vicinity of the studied area, hence they were still relatively fresh and had little S or Cl content especially under low relative humidity conditions.

If we plot average atomic fractions separately for S and Cl as in Fig. 6 (not shown), the overall dependence on relative humidity does not change but the plots become somewhat scattered in vertical sense, suggesting that the distribution of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  on dust particles is competitive or exclusionary in nature as suggested by Sullivan et al. (2007a, b).

#### 4.4 The influence of composition on the CCN activity of mineral dust

As mentioned earlier, the majority of the coarse particles ( $D_p > 1 \mu\text{m}$ ) collected via CVI in this study were dust particles. The probability of the interstitial dust particles contaminating the CVI samples being small indicates that most of the coarse particles collected by the CVI were extracted from the actual cloud droplets. The remaining question is then whether or not all dust particles had the similar potential to act as CCN.

If we compare the relative abundance of silicate (Quartz, Feldspar, Mica, Clay, Amphibole, etc.) and carbonate (Calcite and Dolomite) fractions of dust particles collected via CAI in clear-sky conditions, the silicate particles are usually predominant while carbonate particles occupy on average around  $28 \pm 11\%$  (Fig. 7 upper left). This range of carbonate/(carbonate+silicate) number ratio is also comparable to those typically found in various Asian dust source regions (Trochine et al., 2003; Okada and Kai,

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1995), as well as in the Saharan dust plumes arriving at Tenerife island (Kandler et al., 2007). Interestingly, there were few flights where the carbonate fraction exceeded 60% in the CVI samples (in-cloud) while silicate remained predominant in the adjacent clear-sky layers (silicate<carbonate cases: 06 and 14 August). These cases indicate  
5 that carbonate particles, which readily reacts with acidic gases and deliquesce in the atmosphere, may act primarily as CCN leaving less soluble silicates interstitial.

On the other hand, there were also CVI samples which had similar carbonate/(carbonate+silicate) ratios as in clear-sky samples (silicate>carbonate cases: 04a, 04b, 13 and 17 August). Higher supersaturations may facilitate nucleation on smaller  
10 or less soluble particles. In general, larger updraft velocities result in higher supersaturations. However, updraft velocities measured during the CVI sampling were similar in both “silicate<carbonate” and “silicate>carbonate” cases (about  $0.5 \text{ m s}^{-1}$ ). Although clouds are often highly heterogeneous in space causing fluctuations in the cloud parameters recorded by the Fast Forward Scattering Spectrometer Probe (Burnet and Brenguier, 2002), the mean cloud droplet diameters were mostly around  $10 \mu\text{m}$ , and the liquid water content generally remained below  $<0.1 \text{ gm}^{-3}$  in both cases. Thus, there was no apparent difference in the cloud parameters between the “silicate<carbonate” and “silicate>carbonate” cases.

By comparing the average atomic fraction of S and Cl contained in the silicate  
20 particles in both cases, an interesting trend can be found. The “silicate>carbonate” cases had apparently higher concentration of S+Cl associated with the silicate particles (Fig. 7). It is also interesting to note that the stratocumulus clouds were relatively uniform in “silicate>carbonate” cases whereas more patchy and broken in “silicate<carbonate” cases. This is also reflected in the average relative humidity measured in each CVI operation, where more continuous cloud tends to give relative humidity closer to 100% (Fig. 7).  
25

There may be several explanations for finding “silicate>carbonate” particles in the observed clouds:

1. Silicate particles previously acquired more hygroscopic coatings as indicated by



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the larger S+Cl content, which facilitated their activation.

2. Clouds in “silicate>carbonate” cases experienced slightly higher supersaturations than the “silicate<carbonate” cases, which lead to the activation of not only the carbonate but also less soluble silicate particles. If this was the case, the higher S+Cl content may rather be due to the accelerated uptake after incorporation in cloud droplets.
3. Insoluble dust particles may also be incorporated into cloud droplets due to coagulation.

Scavenging of interstitial aerosol by cloud droplets due to particle diffusion is highly efficient for removing nanometer sized particles which takes place within a matter of few minutes, but takes days for super micron particles (Seinfeld and Pandis, 1998). Instead, in order to test the probability of interstitial dust particles ( $D_p=2\ \mu\text{m}$ , particle density  $2.7\ \text{g cm}^{-3}$ ) colliding with the cloud droplets ( $D_p=10\ \mu\text{m}$ , droplet concentration  $200\ \text{cm}^{-3}$ ), coagulation coefficients  $K\ (\text{m}^3\text{s}^{-1})$  in the turbulent flow regime were calculated after Saffman and Turner (1956). The turbulent energy dissipation rates of  $10^{-4}$  to  $10^{-1}\ \text{m}^2\ \text{s}^{-3}$  were assumed which are typically found in stratocumulus and non-precipitating cumulus clouds (Kitchen and Caughey, 1981; Caughey et al., 1982; Smith and Jonas, 1995). The life time of a dust particle in the cloud estimated based on the coagulation coefficient is about 7.5 h even under a rather turbulent condition with turbulent energy dissipation rate of  $0.1\ \text{m}^2\ \text{s}^{-3}$ . This may be too long as compared to the average residence times of air parcels in clouds, which is said to be of the order of an hour. Considering the similar updraft velocities between the “silicate>carbonate” and “silicate<carbonate” cases, it is unlikely that the clouds in either cases were particularly turbulent than the others, and pathway (iii) may not be so efficient in incorporating interstitial silicate particles into the droplets. Absence of internally mixed silicate and sea salt particles may also indicate slow scavenging of the coarse particles.

Then, the remaining question would be “which came first, the coating or the activation?”. The more uniform cloud and thus higher relative humidity in “silicate>carbonate”

cases suggests larger water vapor content in the atmosphere, which would favor both the relative humidity dependent processing of silicate particles (i), as well as slightly higher supersaturation reached upon the cloud activation (ii). In any case, current results highlight the potential differences in the CCN activities of silicate and carbonate particles, especially in the activation of shallow stratocumulus clouds under relatively calm conditions (i.e. very low supersaturations).

## 5 Conclusions

In this study, individual particle analysis was applied on the actual cloud residues collected in-situ by the airborne CVI. The morphology and mixing states of the cloud residues were directly compared with those of the clear-sky aerosols collected immediately adjacent to the cloud layer. This approach was proved effective in characterizing the CCN fraction of aerosols as well as the influence of cloud processing.

Although the CCN activity of dust particles has been significantly overlooked due to the generally supposed insolubility of silicates, many coarse dust particles were found as cloud residues over the Sahelian region during the summer monsoon period. There was a sharp contrast between the dust particles found in and out of the cloud in terms of the detection frequencies and amount of associated secondary acidic species (sulfate, chloride, nitrate). It is a clear demonstration that the uptake coefficients of acidic gases on dust particles are dependent firstly on the relative humidity, and then they are drastically enhanced upon incorporation into cloud droplets. As a consequence, the employment of relative humidity dependent uptake coefficients is strongly recommended in the global aerosol models for the improved representation of the mineral dust. Since CCN particles may undergo on average ten evaporation/condensation cycles before they finally precipitate in droplets (Pruppacher and Jaenicke, 1995), the amount of and duration in clouds along the dust transport pathways can have significant impact both on the dust composition itself as well as on the atmospheric chemistry (Dentener et al., 1996; Bauer and Koch, 2005).

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Surprisingly large portion of carbonate rich particles were found in a characteristic spherical shape most probably following the uptake of  $\text{HNO}_3$  gas. Since almost all the carbonate particles were forming spherical shapes (even outside of the clouds and away from any significant anthropogenic emission source), it is concluded that such dramatic phase transition readily takes place in the atmosphere even without the presence of cloud processing and heavy pollution.

Due to their alkaline nature, carbonate particles were found particularly reactive at presence of acidic gases, as compared to silicate particles. Although silicate and carbonate particles share the same emission sources and thus are grouped together as “mineral dust”, their behavior is completely different given their reactivity and the ability to readily deliquesce in the atmosphere. This mineralogical diversity of dust particles certainly deserves much more attention from the atmospheric modeling community since the optical properties as well as the interaction with clouds/water cycles is far from being uniform for different kind of dust particles, which in addition are modified due to atmospheric processing.

Kelly et al. (2007) predicted that for dust particles between roughly  $0.6$  and  $2 \mu\text{m}$ , the presence of slightly soluble components can induce activation of dust particles that would not activate if entirely insoluble. Indeed, carbonate particles were found to be significantly enriched in some cloud residual samples, suggesting their primary role as CCN. Instead, when silicate particles were found dominant in cloud residues, they were found to contain more S and Cl elements. Thus, it can be interpreted that, either the silicate particles also play an active role as CCN especially when they are previously coated with hygroscopic coatings, or they simply require higher supersaturation in the initial activation and acquire coatings later due to cloud processing. In any case, current in-situ measurement suggested that the CCN activity of dust particles significantly depend on the chemistry even in the supermicron sizes ( $D_p > 1 \mu\text{m}$ ). This is in contradiction to the argument that the CCN activities of aerosols are determined mainly by size and particle chemistry plays a secondary role (Dusek et al., 2006). Previously, such relative importance of the particle size against the chemistry

was discussed mainly based on the CCN efficiency spectra measured under relatively high supersaturations (0.25–2%). However, ambient supersaturations are usually less than 1% and almost never exceed 2%, and it is said to be typically around 0.1%. In particular, the maximum supersaturation expected in stratocumulus clouds such as the ones we encountered with updraft velocities 0–1 m s<sup>-1</sup> can be as low as 0.05% (Seinfeld and Pandis, 1998). Considering the significance of the stratocumulus clouds in the total cloud coverage of the earth, particle chemistry (and in particular, particle surface chemistry) should also be an important factor controlling the particles' role as CCN.

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- Albrecht, B. A.: Aerosols, cloud microphysics, and fractional cloudiness, *Science*, 245, 1227–1229, 1989.
- Archuleta, C. M., DeMott, P. J., and Kreidenweis, S. M.: Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures, *Atmos. Chem. Phys.*, 5, 2617–2634, 2005, <http://www.atmos-chem-phys.net/5/2617/2005/>.
- Artaxo, P. Martins, J. V., Yamasoe, M. A., Procopio, A. S., Pauliquevis, T. M., Andreae, M. O., Guyon, P., Gatti, L. V., and Leal, A. M. C.: Physical and chemical properties of aerosols in the wet and dry seasons in Rondônia, Amazonia, *J. Geophys. Res.*, 107(D20), 8081, doi:10.1029/2001JD000666, 2002.
- Baltensperger, U. and Nyeki S.: Atmospheric aerosols, Physical and chemical properties of aerosols, edited by: Colbeck, I., Blackie Academic&Professional, 281–330, 1997.
- Bauer, S. E. and Koch, D.: Impact of heterogeneous sulfate formation at mineral dust surfaces on aerosol loads and radiative forcing in the Goddard Institute for Space Studies general circulation model, *J. Geophys. Res.*, 110, D17202, doi:10.1029/2005JD005870, 2005.
- Brandt, C. and Vaneldik, R.: Transition-metal-catalyzed oxidation of sulfur(IV) oxides – atmospheric-relevant processes and mechanisms, *Chem. Rev.*, 95(1), 119–190, 1995.
- Burnet, F. and Brenguier, J.-L.: Comparison between standard and modified Forward Scattering Spectrometer Probes during the Small Cumulus Microphysics Study, *J. Atmos. Ocean. Tech.*, 19, 1516–1531, 2002.
- Caughey, S. J., Crease, B. A., and Roach, W. T.: A field study of nocturnal stratocumulus: il, Turbulence structure and entrainment, *Q. J. Roy. Meteor. Soc.*, 108, 125–144, 1982.
- Cook, K. H.: Generation of the African Easterly Jet and its role in determining West African precipitation, *J. Climate*, 12, 1165–1184, 1999.
- DeMott, P. J., Sassen, K., Poellot, M. R., Baumgardner, D., Rogers, D. C., Brooks, S. D., Prenni, A. J., and Kreidenweis, S. M.: African dust aerosols as atmospheric ice nuclei, *Geophys. Res. Lett.*, 30(14), 1732, doi:10.1029/2003GL017410, 2003.
- Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J., and Crutzen, P. J.: Role of mineral aerosol as a reactive surface in the global troposphere, *J. Geophys. Res.*, 101(D17), 22869–22880, 1996.
- Glugli, R., Jordan, S., and Lindemann, E.: The heterogeneous formation of sulfate aerosols in

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the atmosphere, *J. Aerosol Sci.*, 12, 185–190, 1981.

Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F., Hings, S., Jung, D., Borrmann, S., and Andreae, M. O.: Size matters more than chemistry for cloud-nucleating ability of aerosol particles, *Science*, 312, 1375–1378, 2006.

Feingold, G., Cotton, W. R., Kreidenweis, S. M., and Davis, J. T.: The impact of giant cloud condensation nuclei on drizzle formation in stratocumulus: Implications for cloud radiative properties, *J. Atmos. Sci.*, 56(24), 4100–4117, 1999.

Formenti, P., Elbert, W., Maenhaut, W., Haywood, J., and Andreae, M. O.: Chemical composition of mineral dust aerosol during the Saharan Dust Experiment (SHADE) airborne campaign in the Cape Verde region, September 2000, *J. Geophys. Res.*, 108(D18), 8576, doi:10.1029/2002JD002648, 2003.

Ganor, E. and Mamane, Y.: Transport of Saharan dust across the eastern Mediterranean, *Atmos. Environ.*, 16, 581–587, 1982.

Gibson, E. R., Hudson, P. K., and Grassian V. H.: Aerosol chemistry and climate: Laboratory studies of the carbonate component of mineral dust and its reaction products, *Geophys. Res. Lett.*, 33, L13811, doi:10.1029/2006GL026386, 2006.

Gibson, E. R., Hudson, P. K., and Grassian V. H.: Physicochemical Properties of Nitrate Aerosols: Implications for the Atmosphere, *J. Phys. Chem. A*, 110, 11785–11799, 2006.

Goodman, A. L., Bernard, E. T., and Grassian, V. H.: Spectroscopic study of nitric acid and water adsorption on oxide particles: Enhanced nitric acid uptake kinetics in the presence of adsorbed water, *J. Phys. Chem. A*, 105, 6443–6457, 2001.

Hansch, F. and Crowley, J. N.: Heterogeneous reactivity of gaseous nitric acid on Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, and atmospheric dust samples: A Knudsen cell study, *J. Phys. Chem. A*, 105(13), 3096–3106, 2001.

Hara, K., Osada, K., Nishita, C., Yamagata, S., Yamanouchi, T., Herber, A., Matsunaga, K., Iwasaka, Y., Nagatani, M., and Nakata, H.: Vertical variations of sea-salt modification in the boundary layer of spring Arctic during the ASTAR 2000 campaign, *Tellus*, 54B, 361–376, 2002.

Haywood, J., Francis, P., Osborne, S., Glew, M., Loeb, N., Highwood, E., Tanré, D., Myhre, G., Formenti, P., and Hirst, E.: Radiative properties and direct radiative effect of Saharan dust measured by the C-130 aircraft during SHADE: I. Solar spectrum, *J. Geophys. Res.*, 108, 8577, doi:10.1029/2002JD002687, 2003.

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- Heintzenberg, J., Okada, K., and Ström, J.: On the composition of non-volatile material in upper tropospheric aerosols and cirrus crystals, *Atmos. Res.*, 41, 81–88, 1996.
- Isawa, Y. and Ono, A.: Nitron thin film method for detection of submicron nitrate particles and its application to atmospheric aerosols, *J. Meteorol. Soc. Jpn.*, 57(6), 599–606, 1979.
- 5 Huary, G., Jordan, S., and Hofmann, C.: Experimental investigation of the aerosol-catalyzed oxidation of SO<sub>2</sub> under atmospheric conditions, *Atmos. Environ.*, 12, 281–287, 1978.
- Isono, K., Komabayashi, M., and Ono, A.: The nature and the origin of ice nuclei in the atmosphere, *J. Meteorol. Soc. Jpn.*, 37, 211–233, 1959.
- Ivanov, V. P., Kochubey, D. I., Kutzenogii, K. P., and Bufetov, N. S.: Surface composition of atmospheric aerosols, *React. Kinet. Catal. L.*, 64, 97–102, 1998.
- 10 Kandler, K., Benker, N., Bundke, U., Cuevas, E., Ebert, M., Knippertz, P., Rodriguez, S., Schutz, L., and Weinbruch, S.: Chemical composition and complex refractive index of Saharan Mineral dust at Izana, Tenerife (Spain) derived by electron microscopy, *Atmos. Environ.*, 41, 8058–8074, 2007.
- 15 Kelly, J. T. and Wexler, A. S.: Thermodynamics of carbonates and hydrates related to heterogeneous reactions involving mineral aerosol, *J. Geophys. Res.*, 110, D11201, doi:10.1029/2004JD005583, 2005.
- Kelly, J. T., Chuang, C. C., and Wexler, A. S.: Influence of dust composition on cloud droplet formation, *Atmos. Environ.*, 41, 2904–2916, 2007.
- 20 Kitchen, M. and Caughey, S. J.: Tethered-balloon observations of the structure of small cumulus clouds, *Q. J. Roy. Meteor. Soc.*, 107, 853–874, 1981.
- Krueger, B. J., Grassian, V. H., Laskin, A., and Cowin, J. P.: The transformation of solid atmospheric particles into liquid droplets through heterogeneous chemistry: Laboratory insights into the processing of calcium containing mineral dust aerosol in the troposphere, *Geophys. Res. Lett.*, 30(3), 1148, doi:10.1029/2002GL016563, 2003.
- 25 Krueger, B. J., Grassian, V. H., Cowin, J. P., and Laskin, A.: Heterogeneous chemistry of individual mineral dust particles from different dust source regions: the importance of particle mineralogy, *Atmos. Environ.*, 38, 6253–6261, 2004.
- Laskin, A., Iedema, M. J., Ichkovich, A., Graber, E. R., Taraniuk, I., and Rudich, Y.: Direct observation of completely processed calcium carbonate dust particles, *Faraday Discuss.*, 130, 453–468, 2005.
- 30 Levin, Z., Ganor, E., and Gladstein, V.: The effects of desert particles coated with sulfate on rain formation in the Eastern Mediterranean, *J. Appl. Meteorol.*, 35, 1511–1523, 1996.

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Li, J., Pósfai, M., Hobbs, P. V., and Buseck, P. R.: Individual aerosol particles from biomass burning in southern Africa: 2. Compositions and aging of inorganic particles, *J. Geophys. Res.*, 108(D13), 8484, doi:10.1029/2002JD002319, 2003.

Lohmann, U., Kärcher, B., and Hendricks, J.: Sensitivity studies of cirrus clouds formed by heterogeneous freezing in the ECHAM GCM, *J. Geophys. Res.*, 109, D16204, doi:10.1029/2003JD004443, 2004.

Matsuki, A., Iwasaka, Y., Shi, G. Y., Chen, H. B., Osada, K., Zhang, D., Kido, M., Inomata, Y., Kim, Y. S., Trochkin, D., Nishita, C., Yamada, M., Nagatani, T., Nagatani, M., and Nakata, H.: Heterogeneous sulfate formation on dust surface and its dependence on mineralogy: Balloon-borne measurements in the surface atmosphere of Beijing, China, *Water Air Soil Poll.*, Focus, 5, 101–132, 2005a.

Matsuki, A., Iwasaka, Y., Shi, G. Y., Zhang, D. Z., Trochkin, D., Yamada, M., Kim, Y. S., Chen, B., Nagatani, T., Miyazawa, T., Nagatani, M., and Nakata, H.: Morphological and chemical modification of mineral dust: Observational insight into the heterogeneous uptake of acidic gases, *Geophys. Res. Lett.*, 32(22), L22806, doi:10.1029/2005GL024176, 2005b.

Mouri, H., Nagao, I., Okada, K., Koga, S., and Tanaka, H.: Elemental composition of individual aerosol particles collected from the coastal marine boundary layer, *J. Meteorol. Soc. Jpn.*, 74, 585–591, 1996.

Ogren, J. A., Heintzenberg J., and Charlson R. J.: In-situ sampling of clouds with a droplet to aerosol converter, *Geophys. Res. Lett.*, 12, 121–124, 1985.

Okada, K. and Kai, K.: Features and elemental composition of mineral particles collected in Zhangye, China, *J. Meteorol. Soc. Jpn.*, 73(5), 947–957, 1995.

Ooki, A. and Uematsu, M.: Chemical interactions between mineral dust particles and acid gases during Asian dust events, *J. Geophys. Res.*, 110, D03201, doi:10.1029/2004JD004737, 2005.

Pruppacher, H. R. and Jaenicke, R.: The processing of water vapor and aerosols by atmospheric clouds, a global estimate, *Atmos. Res.*, 38, 283–295, 1995.

Rosenfeld, D., Rudich, Y., and Lahav, R.: Desert dust suppressing precipitation: A possible desertification feedback loop, *P Natl. Acad. Sci. USA*, 98(11), 5975–5980, 2001.

Saffman, P. G. and Turner, J. S.: On the collision of drops in turbulent clouds, *J. Fluid Mech.*, 1, 16–30, 1956.

Sassen, K., DeMott, P. J., Prospero, J. M., and Poellot, M. R.: Saharan dust storms and indirect aerosol effects on clouds: CRYSTAL-FACE results, *Geophys. Res. Lett.*, 30, 1633,



doi:10.1029/2003GL017371, 2003.

Schwarzenboeck, A. and Heintzenberg, J.: Cut size minimization and cloud element break-up in a ground-based CVI, *J. Aerosol Sci.*, 31, 477–489, 2000.

Schwarzenboeck, A., Heintzenberg, J., and Mertes, M.: Incorporation of aerosol particles between 25 and 850 nm into cloud elements: measurements with a new complementary sampling system, *Atmos. Res.*, 52, 241–260, 2000.

Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Wiley, New York, USA, 1998.

Smith, S. A. and Jonas, P. R.: Observations of the turbulent fluxes in fields of cumulus clouds, *Q. J. Roy. Meteor. Soc.*, 121, 1185–1208, 1995.

Sokolik, I., Winker, D. M., Bergametti, G., Gillette, D. A., Carmichael, G., Kaufman, Y., Gomes, L., Schuetz, L., and Penner, J. E.: Introduction to special section: outstanding problems in quantifying the radiative impacts of mineral dust, *J. Geophys. Res.*, 106, 18015–18028, 2001.

Stewart, D. J., Taylor, C. M., Reeves, C. E., and McQuaid, J. B.: Biogenic nitrogen oxide emissions from soils: impact on NO<sub>x</sub> and ozone over west Africa during AMMA (African Monsoon Multidisciplinary Analysis): observational study, *Atmos. Chem. Phys.*, 8, 2285–2297, 2008, <http://www.atmos-chem-phys.net/8/2285/2008/>.

Sullivan, R. C., Guazzotti, S. A., Sodeman, D. A., and Prather, K. A.: Direct observations of the atmospheric processing of Asian mineral dust, *Atmos. Chem. Phys.*, 7, 1213–1236, 2007a, <http://www.atmos-chem-phys.net/7/1213/2007/>.

Sullivan, R. C., Guazzotti, S. A., Sodeman, D. A., Tang, Y., Carmichael, G. R., and Prather, K. A.: Mineral dust is a sink for chlorine in the marine boundary layer, *Atmos. Environ.*, 41, 7166–7179, 2007b.

Tanaka, T. Y. and Chiba, M.: Global simulation of dust aerosol with a chemical transport model MASINGAR, *J. Meteorol. Soc. Jpn.*, 83A, 255–278, 2005.

Tang, I. N. and Fung, K. H.: Hydration and Raman scattering studies of levitated microparticles: Ba(NO<sub>3</sub>)<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub>, *J. Chem. Phys.*, 106(5), 1653–1660, 1997.

Trochikine, D., Iwasaka, Y., Matsuki, A., Yamada, M., Kim, Y. S., Nagatani, T., Zhang, D., Shi, G. Y., and Shen, Z.: Mineral aerosol particles collected in Dunhuang, China, and their comparison with chemically modified particles collected over Japan, *J. Geophys. Res.*, 108(D23), 8642, doi:10.1029/2002JD003268, 2003.

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9, 1797–1830, 2009

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Twohy, C. H. and Poellot, M. R.: Chemical characteristics of ice residual nuclei in anvil cirrus clouds: evidence for homogeneous and heterogeneous ice formation, *Atmos. Chem. Phys.*, 5, 2289–2297, 2005, <http://www.atmos-chem-phys.net/5/2289/2005/>.

- 5 Twomey, S.: Pollution and the planetary albedo, *Atmos. Environ.*, 8, 1251–1256, 1974.
- Underwood, G. M., Song, C. H., Phadnis, M., Carmichael, G. R., and Grassian, V. H.: Heterogeneous reactions of NO<sub>2</sub> and HNO<sub>3</sub> on oxides and mineral dust: A combined laboratory and modeling study, *J. Geophys. Res.*, 106(D16), 18055–18066, 2001.
- 10 Usher, C. R., Al-Hosney, H., Carlos-Cueller, S., and Grassian, V. H.: A laboratory study of the heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles, *J. Geophys. Res.*, 107(D23), 4713, doi:10.1029/2003JD004309, 2002.
- Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on mineral dust, *Chem. Rev.*, 103(12), 4883–4939, 2003.
- 15 Vlasenko, A., Sjogren, S., Weingartner, E., Stemmler, K., Gäggeler, H. W., and Ammann, M.: Effect of humidity on nitric acid uptake to mineral dust aerosol particles, *Atmos. Chem. Phys.*, 6, 2147–2160, 2006, <http://www.atmos-chem-phys.net/6/2147/2006/>.
- Wu, P.-M. and Okada, K.: Nature of coarse nitrate particles in the atmosphere-A single particle approach, *Atmos. Environ.*, 28, 2053–2060, 1994.
- 20 Zhang, D. and Iwasaka, Y.: Chlorine deposition on dust particles in marine atmosphere, *Geophys. Res. Lett.*, 28, 3613–3616, 2001.
- Zhu, X., Prospero, J. M., Millero, F. J., Savoie, D. L., and Brass, G. W.: The solubility of ferric ion in marine mineral aerosol solutions at ambient relative humidities, *Mar. Chem.*, 38(1–2), 91–107, 1992.

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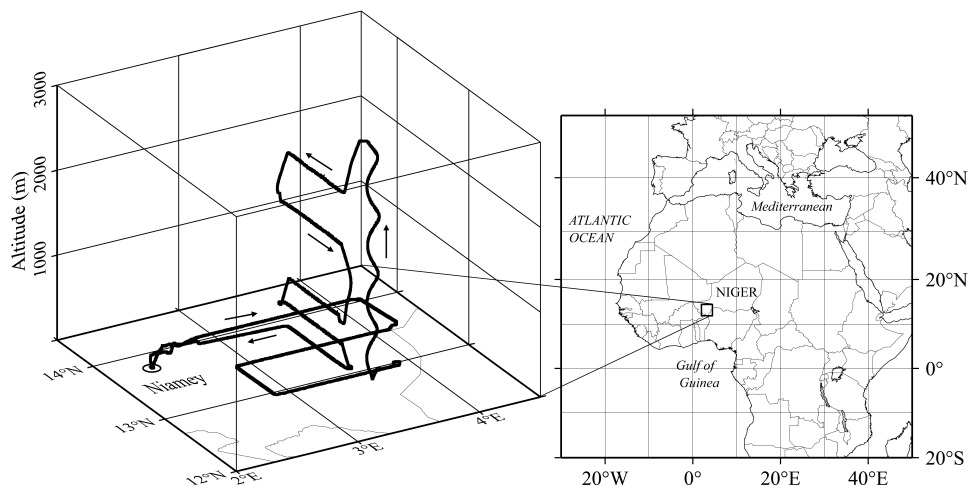
**Table 1.** Mineral classification of individual dust particles based on the elemental composition (atomic fraction, %).

Groups		Classification criteria	Mineralogy deduced from elemental composition
1	Quartz	Si>85%	Quartz
2	Aluminosilicate I	not in other classes	Clay (kaolinite, smectite, illite), mica (muscovite, biotite), feldspar
3	Aluminosilicate II	Ti>3% or Fe/Si>1 or (Mg+Fe)/Al>1 and K<3% and Mg/Si<1	Amphibole, hematite, anatase
4	Calcite	Si/Ca<1 and Mg/Ca<0.5	Calcite, gypsum
5	Dolomite	Si/Ca<1 and Mg/Ca>0.5	Dolomite

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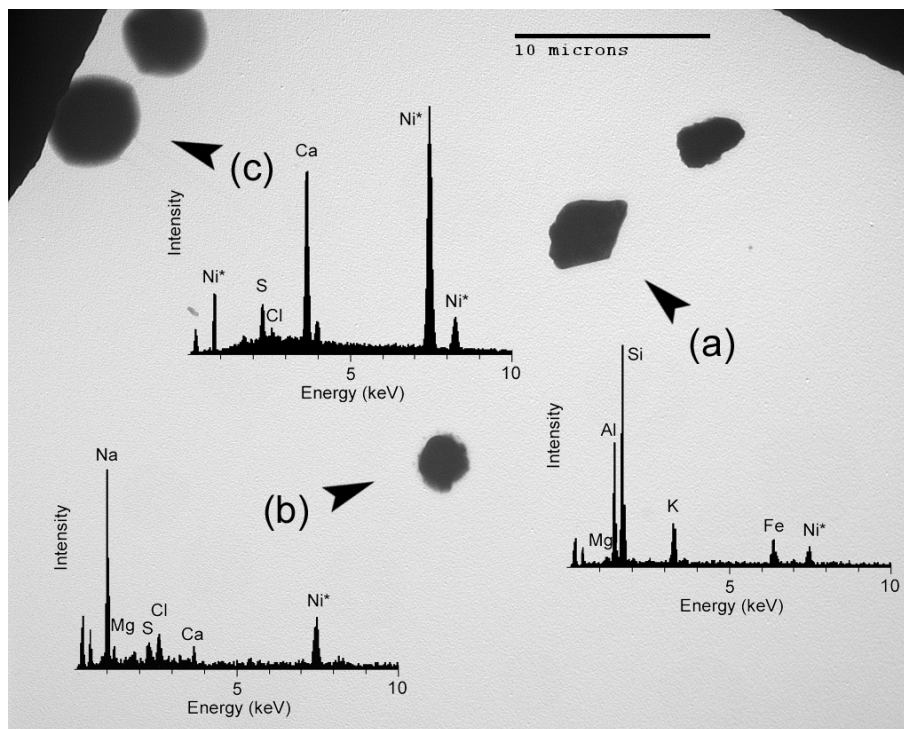
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**Fig. 1.** The geographical location of the measurement area and a representative flight pattern of stacked horizontal legs of the ATR-42 aircraft (from 5 August 2006).

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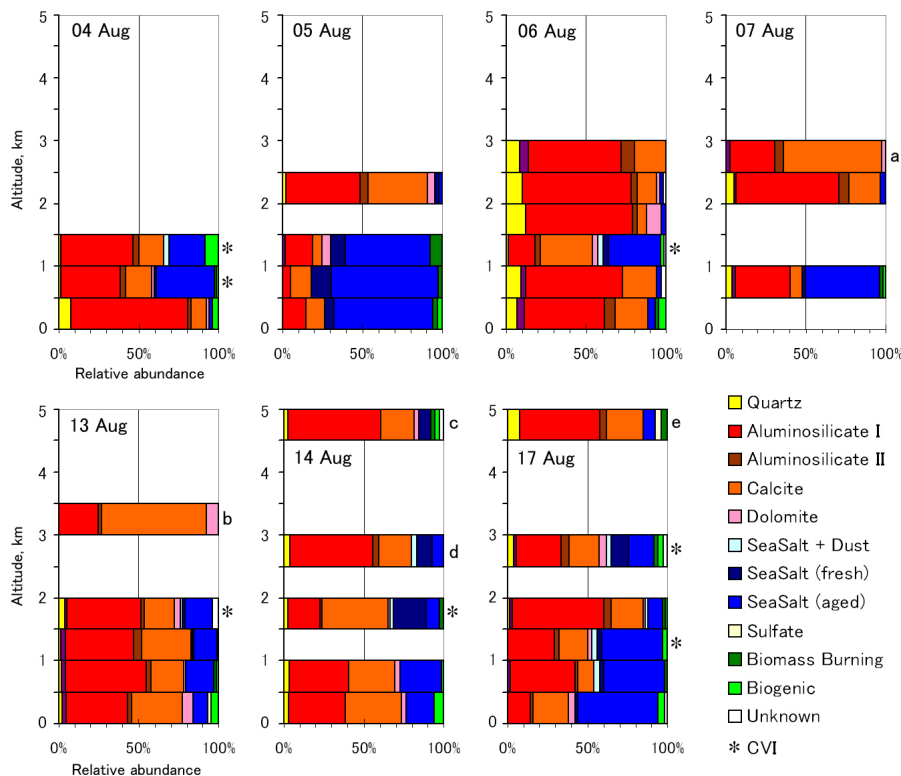
**Fig. 2.** Representative electron micrograph and X-ray spectra of super-micron particles collected via CVI inside a cloud layer on 14 August 2008.

\* Peak of Ni results from the metal film support.

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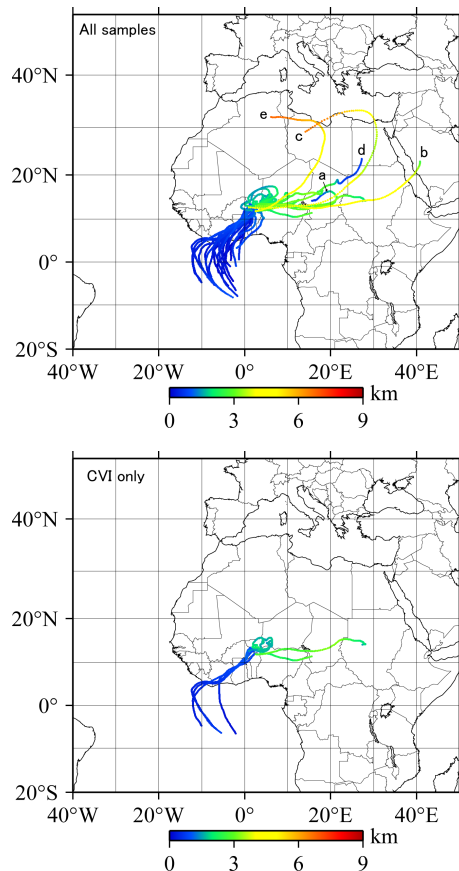


**Fig. 3.** Various types of super-micron particles ( $D_p > 1 \mu\text{m}$ ) and their relative abundance found in the clear-sky and in-cloud samples. Each sample represents a 0.5 km vertical interval in which it was sampled. In-cloud (CVI) samples are indicated by the asterisks (\*). Characters **(a)** to **(e)** relate selection of samples to the peculiar air-mass trajectories shown subsequently in Fig. 4.

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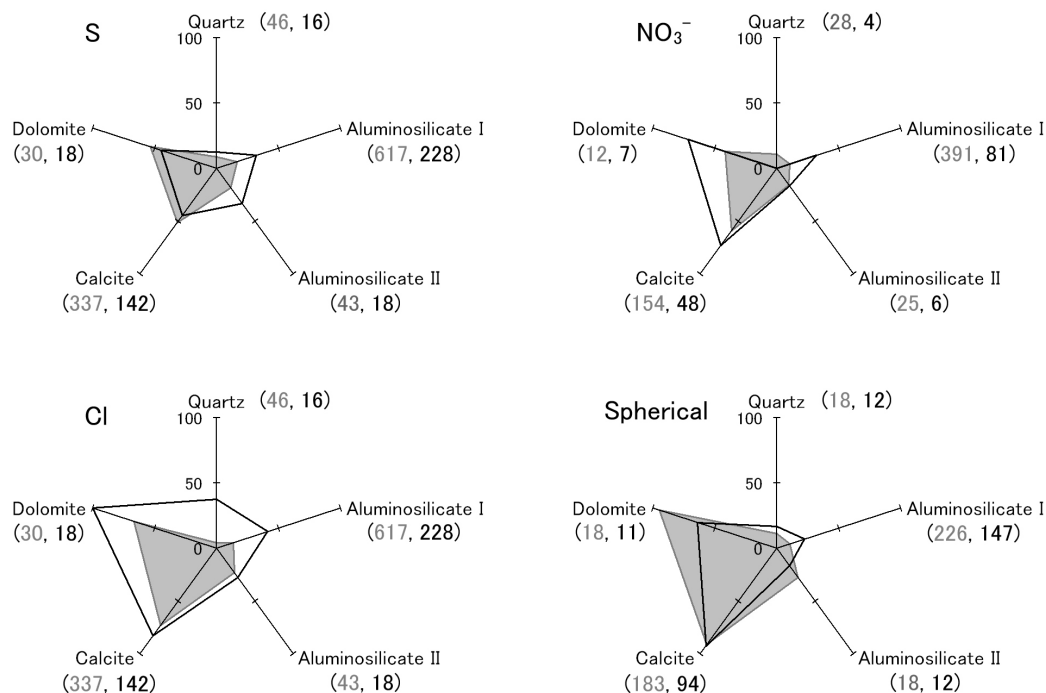


**Fig. 4.** The 5-day air-mass backward trajectories arriving at the point of collection for all the samples (upper graph), and extraction of in-cloud (CVI) samples only (lower graph). Several peculiar trajectories are labeled by the characters **(a)** to **(e)**.

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**Fig. 5.** Detection frequencies of S and Cl elements (by SEM-EDX) as well as NO<sub>3</sub><sup>-</sup> ion (using nitron reagent film) among the individual mineral dust particles of different mineralogy. Fractions of particles resembling spherical particles (Fig. 2c) are also compared. The Fe rich and Ti containing fraction (Aluminosilicate II) was distinguished from the major aluminosilicate particles (Aluminosilicate I) for comparison. The detection frequencies are compared between the clear-sky (gray area) and in-cloud (solid black line) samples. The absolute numbers of total investigated particles from the clear-sky (gray) and in-cloud (black) samples are indicated in the parenthesis.

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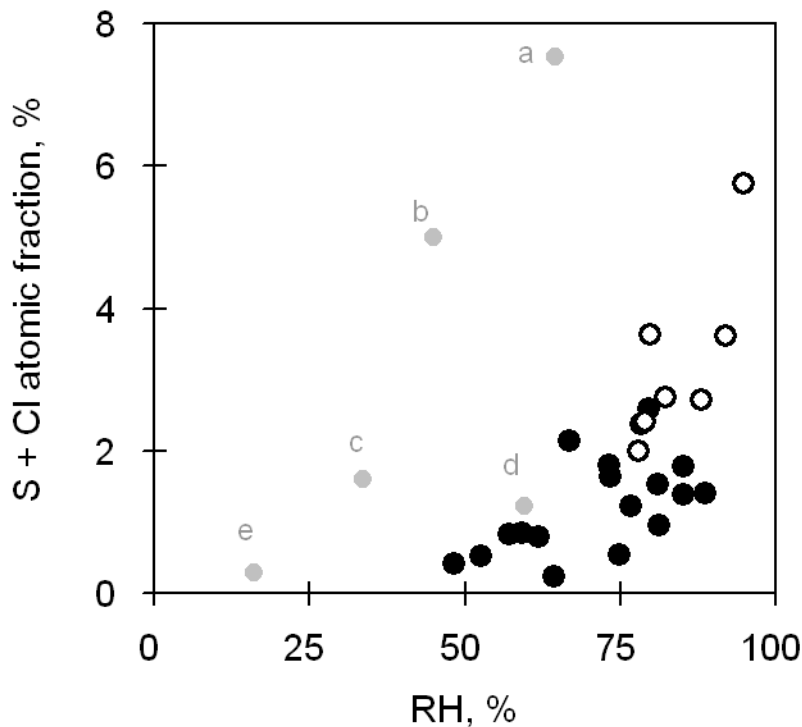
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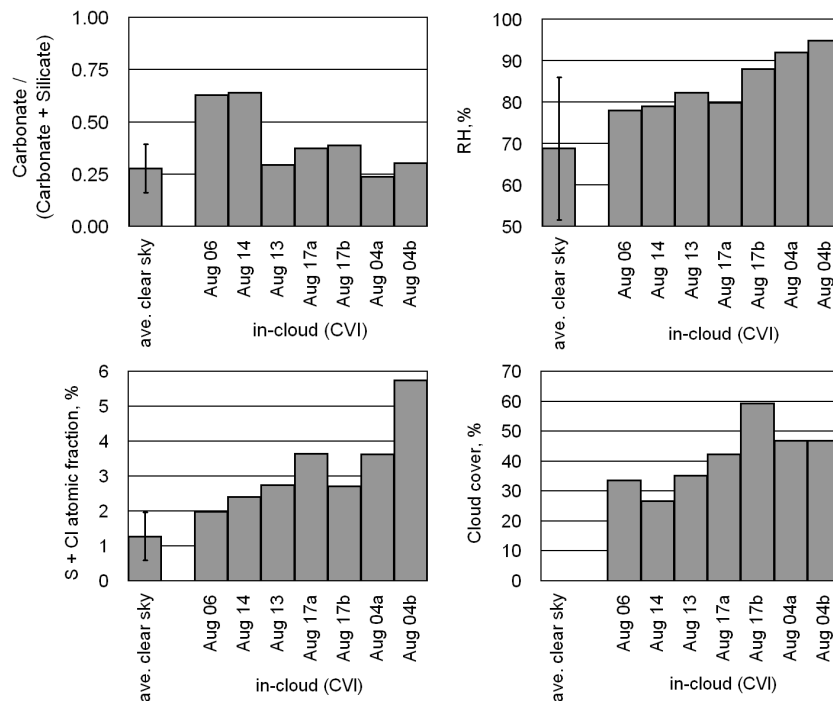


**Fig. 6.** The sum of average S and Cl atomic fractions in the silicate particles (Quartz, Aluminosilicate I+II) plotted against the relative humidity at which the sample was collected. Samples collected in-cloud (open circles) were distinguished from the clear-sky samples (filled circles). Characters **(a)** to **(e)** relate the samples to the peculiar air-mass trajectories shown in Fig. 4.

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**Fig. 7.** Number ratios of carbonate particles relative to the total mineral dust particles (Carbonate/Carbonate+Silicate) found in cloud samples are compared with the average ratio in the clear-sky conditions (upper left). The error bar indicates one standard deviation. Also shown are the average S+Cl atomic fractions found in the silicate particles (lower left), relative humidity at the time of sampling (upper right), and the cloud cover along the flight track (lower right). The cloud cover is deduced from the fraction of time in which significant count of cloud residual particles appeared during a given CVI operation (i.e. 0% in clear-sky and 100% inside a continuous and homogeneous cloud).

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