**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Importance of atmospheric aging in reactivity of mineral dust aerosol: a case study of heterogeneous reaction of gaseous hydrogen peroxide on processed mineral particles" *by* Y. Zhao et al.

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We gratefully thank you for the constructive comments and suggestions. Our point-to-point replies to the individual comments are as follows.

General comments

Zhao et al have examined reactions of H_2O_2 on pre-treated Al_2O_3 surfaces, which have been exposed to nitric acid or SO_2. They discuss the observations of nitrate or sulphate dependent uptake coefficients in terms of a mechanism involving two sorts of

H_2O_2 uptake, one driven by active-sites (dominant at low RH and low nitrate) and one driven by H_2O (dominant at high RH and e.g. high nitrate).

(Q1) Whilst the results show some interesting trends, it is not clear how any of this data or its interpretation can be extrapolated to atmospheric mineral aerosol, which is not Al_2O_3 and which will presumably behave completely differently with respect to uptake of nitrate, SO_2 or H_2O.

(A1) Field measurements have shown that the chemical composition of mineral dust as well as its reactivity can be largely modified as the particles undergo aging during atmospheric transport (Formenti et al., 2011). To qualitatively evaluate the effect of atmospheric aging on the reactivity of mineral dust particles, Saharan and Asian dust appear to be the best choice of the particle samples as these two kinds of dust represent the largest source of mineral dust particles on earth. However, the careful characterization of the physicochemical properties (e.g., composition, particle shape and size) of the authentic dust samples is indispensible to accurately interpret the heterogeneous kinetics. To achieve this, a series of experimental and analytical techniques are necessary. In addition, sample preparation of the authentic dust samples for our transmission-FTIR study is difficult and complicated. Thus, due to the limitation of techniques in our laboratory, we used two reactive compounds of mineral dust, i.e., alumina and calcium carbonate (we have performed a number of H_2O_2 uptake experiments on clean and processed $CaCO_3$ in the revised manuscript after your comments arrived), as surrogates to investigate the effect of atmospheric aging on the reactivity of mineral dust particles. It is well known that calcite ($CaCO_3$, as an important Ca-containing mineral dust in the atmosphere, is especially reactive toward nitrogen oxides (Usher et al., 2003a; Crowley et al., 2010). A number of field studies have observed a strong correlation between dust nitrate and Ca^{2+} (Zhuang et al., 1999; Sullivan et al., 2007; Li et al., 2009). In particular, single particle studies have shown that Ca-containing mineral dust is frequently covered by visible $Ca(NO_3)_2$ coatings mainly through the reaction with HNO_3 (Kruegera et al., 2004; Li et al., 2009). Alumina, a major reactive component of

aluminium silicate, generally comprises 10–15% of the total dust loading (Usher et al., 2003a). Compared to Ca-containing dust, aluminium silicate particles are much less reactive toward nitrogen oxide, whereas good correlations between nitrate and Al in dust plumes have also been reported (Sun et al., 2005). In addition, aluminium silicate particles seem to be more closely associated with sulfate formation on atmospheric mineral dust (Sullivan et al., 2007; Formenti et al., 2011). Thus, processed calcium carbonate and alumina particles, to various degrees, can be used as models for ambient aged mineral dust, and the results of this study will help us to understand the evolution of the reactivity of mineral dust particles upon atmospheric aging.

The following statement has been added to the Introduction of the revised manuscript.

"Here, calcium carbonate ($CaCO_3$) and alumina (α-Al_2O_3)were selected as substrates as a result of their abundance in atmospheric mineral dust aerosol and their affinity for acidic trace gases. For example, $CaCO_3$ (calcite) particles, an important Ca-containing mineral dust, can make up as much as 20–30% of the total dust loading (Claquin et al., 1999; Kandler et al., 2009) and are well known to be highly reactive toward HNO_3 and nitrogen oxides (Usher et al., 2003a; Crowley et al., 2010). A number of field and model studies have observed a strong correlation between dust nitrate and calcium ions (Zhuang et al., 1999; Song and Carmichael, 2001; Sullivan et al., 2007; Li et al., 2009). In particular, single particle studies have shown that Ca-containing mineral dust is frequently covered by visible $Ca(NO_3)_2$ coatings mainly through the reaction with HNO_3 (Kruegera et al., 2004; Li et al., 2009). Alumina, a major reactive component of aluminium silicate, generally comprises 10–15% of the total dust loading (Usher et al., 2003a). Compared to Ca-containing dust, aluminium silicate particles are much less reactive toward nitrogen oxide, whereas good correlations between nitrate and Al in dust plumes have also been reported (Sun et al., 2005). In addition, aluminium silicate particles seem to be more closely associated with sulfate formation on atmospheric mineral dust (Sullivan et al., 2007; Formenti et al., 2011). In view of this, calcium carbonate and alumina, to various degrees, can be used as models to begin to understand

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the evolution of the reactivity of mineral dust aerosol upon atmospheric aging."

In addition, the following statement has been added to the Conclusion and Atmospheric Implication of the revised manuscript.

"It should be noted that the HNO_3 and SO_2-processed α-Al_2O_3 and $CaCO_3$ particles used in this study to investigate the effects of atmospheric aging are simple models for ambient aged mineral dust, which has far more complicated physicochemical properties (e.g., composition, mixing state, shape, and size). However, our results presented here do suggest that mineral dust aged in the atmosphere have distinct reactivity relative to the freshly emitted mineral particles and behaves differently with respect to the uptake of trace gases. Furthermore, the importance of atmospheric aging on the reactivity is intimately linked to the mineral composition of dust particles. To better understand the role of mineral dust in atmospheric chemistry, the effects of atmospheric aging should be included in the atmospheric models which currently in general employ the uptake coefficients derived on unaged mineral particles (Bauer et al., 2004; Zhu et al., 2010)." In the revised manuscript, we have performed a number of additional experiments on HNO_3 treated $CaCO_3$ particles with varying coverage of nitrate (1–10 monolayer), as well as on SO_2 treated $CaCO_3$ surface with sulfite coverage of 50% monolayer, and we have observed far more pronounced effects on processed $CaCO_3$ particles. The results and discussion of H_2O_2 uptake on HNO_3 and SO_2-processed $CaCO_3$ particles have been added to the revised manuscript as seen in Sections 3.2.2 and 3.3.2, and Fig. 6, Figs. 9 to11.

(Q2) The amounts of all trace gases used have little bearing on atmospheric mixing ratios yet there is no discussion or supportive data (e.g. experiments at various H_2O_2) to convince the reader that the use of lower concentrations would lead to the same conclusions.

(A2) In the revised manuscript, the effects of varying H_2O_2 concentration on the uptake was investigated by conducting measurements over the H_2O_2 concentration range of

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(1.9–18.7) $\times 10^{14}$ molecules cm^{-3} (0.8–7.6 ppmv) at 45% RH. As shown in Fig.12 in the revised manuscript, the uptake coefficients of H_2O_2 on HNO_3 and SO_2-processed particles appear to be independent of H_2O_2 concentration. This implies that the uptake behaviors of the processed mineral particles measured here may be also applicable to lower H_2O_2 concentrations that are more relevant to the atmosphere.

(Q3) The methodology used is known to generate uptake coefficients which may be orders of magnitude too low. Indeed, in the conclusions, the authors have to scale their results by a factor 10000 to align them with data measured using dispersed aerosol.

(A3) Indeed, the uptake coefficients obtained on powdered bulk samples is generally several orders of magnitude lower than those derived using dispersed particles, mainly arising from the uncertainty in estimation of effective surface area available for reaction (Crowley et al., 2010). Although our previous work (Zhao et al., 2011) suggested that the BET surface area likely more appropriately represent the effective surface area of the particle sample, the BET uptake coefficients estimated in the present study represent the lower limit of the uptake. However, the main focus of this work was on the effects of atmospheric aging on the reactivity of mineral particles. By conducting H_2O_2 uptake experiments on both clean and processed particles with the same method, we are able to derive the impacts of aging processes on the reactivity of mineral particles toward H_2O_2.

We have added this statement to the Conclusion and atmospheric implication of the revised manuscript.

(Q4) Overall the paper is rather thin, both lacking in detail and seemingly based on few experiments. I would suggest the authors conduct some similar experiments on either Saharan or Asian dust (or a number of different components of mineral aerosol) before publication in an atmospheric science journal.

(A4) Thanks for your suggestion. In the revised manuscript, we have conducted a number of additional H_2O_2 uptake experiments including those on processed $CaCO_3$

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particles and at varying H_2O_2 concentrations. Please see the details in (A1) and (A2) and also in the revised manuscript.

Overall, by fully addressing all concerns both reviewers raised, we have made a significant revision for the manuscript. We believe that the revised manuscript is much improved.

Specific comments

(Q5) P28568, L21 Time dependent H_2O_2 data is used to derive the uptake coefficient using equations 1 and 2. This data should be shown. Also, given the experimental set-up and explanation as to how was the interaction time was calculated should be given.

(A5) Figure 2 in the revised manuscript shows an example of H_2O_2 uptake kinetics by alumina particles at 45% RH and surface nitrate coverage of 3.4 $\times 10^{18}$ molecules m^{-2}. Some loss (less than 5%) of gas-phase H_2O_2 in the absence of particles on grid was observed within the first several min of exposure and then appeared to approach a constant value due to the surface saturation of the wall. By subtracting the wall loss from total loss of gas-phase H_2O_2, the uptake of H_2O_2 by mineral particles can be derived. It can be seen that at the initial exposure stage, the uptake of H_2O_2 increase quickly and linearly, and after several min of exposure (> 10 min), the uptake rate seems to slow down due to the surface deactivation or saturation of particles. Generally, at least three individual experiments were averaged to get H_2O_2 uptake kinetics under each experimental condition. Based on the uptake rate (d{C}/dt) of H_2O_2, which was determined from the linear fit to the time-dependent uptake data within the first 10 min of exposure, the uptake coefficients of H_2O_2 on processed particles were calculated using eqs (1) and (2) (see the revised manuscript).

Figure 1 in the revised manuscript shows schematic diagram of the experimental set-up that consists of three main components: reactor, pumping and gas handling system, and H_2O_2 collection and detection system. The reactor (length 15 cm, ID 3.3 cm)

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is a quartz tube with two infrared windows made of ZnSe. The α-Al$_2$O$_3$ and CaCO$_3$ samples, with typical mass of 15 mg and 23 mg respectively, were evenly placed on a 250-mesh stainless steel circular grid and slightly compressed to form solid coatings, which was then mounted in the center of the reactor. The reactant-containing synthetic air was introduced into the reactor at a constant rate of 400 sccm (corresponding to line speed 0.86 cm s^{-1}). The gas/particle interaction occurred as the trace gas passed through the grid coated with particles. Given the particle sample thickness of 0.14 mm, the contact time between trace gas and surface was estimated to be 0.02 s.

These experimental details have been given in the revised manuscript.

(Q6) P28570, L9 How was the surface nitrate concentration calculated. What assumptions were used. How reliable is this number? The same question applies for the SO$_2$ processed particles and the surface concentration of sulfite or bisulfite. In the nitrate case, the authors mention that liquid-like water may drive the uptake at high RH. But this would surely be evident in the FTIR spectra?

(A6) The surface coverage of coatings was measured with the method as follows: after H$_2$O$_2$ uptake, the processed particle sample was sonicated in 10 ml Milli-Q water (Millipore, USA) to extract surface adsorbed nitrate and sulfate. The resulting solution was then filtered and analyzed using an ion chromatography (Dionex ICS2000, USA), which is equipped with a Dionex AS 11 analytical column and a conductivity detector. In the sulfite (or bisulfite) case, the processed particles were exposed to gaseous H$_2$O$_2$ for enough time to make sure of the complete conversion of sulfite into sulfate, which was monitored using T-FTIR. Assuming surface nitrate and sulfate species are stable during the whole process of H$_2$O$_2$ uptake, the amount of nitrate and sulfate determined using IC was considered to be identical to that of nitrate and sulfite/bisulfite on processed particles. The coverage of coatings was then derived by normalizing the amount of adsorbed ions with the BET surface area of the particle samples.

In our previous work (Zhao et al., 2011), we have found that heterogeneous decompo-

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sition dominates H$_2$O$_2$ uptake on alumina particles, and even at high RH (e.g., 75%) H$_2$O$_2$ decomposition could still account for about 85% of the total uptake of H$_2$O$_2$ by the particles. In the present study, the liquid-like water appears to drive the uptake of H$_2$O$_2$ on nitrated alumina particles at high RH. However, no evident increase in infrared absorption associated with molecularly adsorbed H$_2$O$_2$ can be observed in the FTIR spectra. This suggests that H$_2$O$_2$ molecules taken up by the nitrated particles may also undergo significant decomposition.

We have added the above discussion to the revised manuscript.

(Q7) P28571, 28572 The text on page 28571 (lines 3-18) largely repeats itself on lines (17-29) and on lines 1-11 of the next page.

(A7) In the revised manuscript, these sentences have been rewritten as follows:

"Under dry conditions, the quantity of oxide active sites determines the reactivity of α-Al$_2$O$_3$ toward H$_2$O$_2$ (Zhao et al., 2011), and the HNO$_3$ reaction with α-Al$_2$O$_3$ appears to consume the same active sites for H$_2$O$_2$ uptake. Thus, by occupying surface reactive sites, adsorbed nitrate on α-Al$_2$O$_3$ is expected to decrease the reactivity of the surface. As shown here, at 3% RH, the measured uptake of H$_2$O$_2$ on processed α-Al$_2$O$_3$ decreases from 1.1 $\times10^{-7}$ to 0.7 $\times10^{-7}$ with the surface nitrate coverage increasing from 0 to 3.5 $\times10^{18}$ molecules m^{-2}. Similar deactivation of α-Al$_2$O$_3$ surfaces with adsorbed nitrate was also observed in the study performed by Usher et al. (2003b), with O3 uptake on nitrated α-Al$_2$O$_3$ under dry conditions decreasing by approximately 70% relative to that on uncoated particles. At intermediate RH (e.g., 25%, 45%, and 60%), the presence of adsorbed nitrate at low surface coverage still decreases the reactivity of α-Al$_2$O$_3$ particles toward H$_2$O$_2$ by blocking surface reactive sites. However, the nitrate coating is quite hydrophilic and can largely enhance water adsorption of alumina surfaces under humid conditions, which may favor H$_2$O$_2$ uptake onto surface liquid-like water due to the high solubility of H$_2$O$_2$. Therefore, as the surface nitrate coverage increases, the surface reactivation attributed to the increase of surface hygrophilicity pre-

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vails against the further deactivation of the particles, leading to the recovery of H_2O_2 uptake. At high RH (e.g., 75% and 92%), the presence of nitrate coatings strongly enhances the coverage of liquid-like water on the surface. Thus, via adsorption into the growing content of liquid-like water, H_2O_2 uptake increases with increasing nitrate coverage."

(Q8) P28571 (and Figure 2) When no nitrate is present, the maximum uptake coefficient is found at zero RH. This would seem to contrast the statement that the uptake is driven by available water at high nitrate.

(A8) On clean alumina particles, the uptake of H_2O_2 is determined by the intrinsic chemical reactivity, thus the maximum uptake coefficient on clean alumina is found at zero RH where the particle surface has highest chemical reactivity, whereas on processed alumina particles coated with high nitrate the uptake of H_2O_2 is controlled by the content of surface liquid-like water, hence the increasing RH appears to favor H_2O_2 uptake. A more pronounced effect related to the RH and surface coverage of nitrate can be found on clean and nitrate-coated $CaCO_3$ particles (see A1).

(Q9) P28574, L14-15 6.2 % of the BET surface is covered by a (full) monolayer? Does this imply that the other 94 % has zero S(IV). This is not how adsorption isotherms work. Figure 1 The FTIR traces appear to have been offset. This needs to be stated in the caption.

(A9) The reactivity of alumina particles toward SO_2 is closely linked to the number of active sites (i.e. surface hydroxyl group) on the surface, and the reaction ceases when all of the surface active sites are consumed. Thus, S(IV) species is produced only on the place of the surface active sites available for SO_2 reaction, which only account for a portion of surface area. In the present study, after the reaction of SO_2, only 6.2 % of the BET surface on alumina particles is covered by S(IV) species. The result presented here agrees well with that reported in the literature (Goodman et al., 2001).

We have added the statements "The spectra are offset for clarity" to the caption.

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(Q10) Figure 3 The insets have illegible captions

(A10) We have enlarged the captions in the revised manuscript.

(Q11) Figure 4 How many experiments were averaged to get the uptake coefficient at each RH? How were the error bars derived?

(A11) Generally, at least three individual experiments were averaged to get the uptake coefficients under each experimental condition. The error bars represent one-standard deviation. In the revised manuscript, we have added these statements to the captions.

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