

***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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Received and published: 20 February 2012

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

This paper reports an experimental study of the  $\text{H}_2\text{O}_2$  heterogeneous interaction with  $\text{Al}_2\text{O}_3$  surface. The uptake coefficient of  $\text{H}_2\text{O}_2$  is determined as a function of relative humidity (RH) and surface concentration of nitrate or sulfite. Pretreatment of the alumina surfaces with  $\text{HNO}_3$  and  $\text{SO}_2$  is shown to affect the  $\text{H}_2\text{O}_2$  uptake in a complex

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way: increase or decrease of the uptake coefficient depending on the surface coverage and RH. Possible mechanisms of the  $\text{H}_2\text{O}_2$  interaction with  $\text{HNO}_3$  and  $\text{SO}_2$  processed  $\text{Al}_2\text{O}_3$  surface are discussed.

(Q1) I would limit my review to one major comment concerning the measurement of the uptake coefficient of  $\text{H}_2\text{O}_2$  which was the main objective of this experimental study. In fact, the original experimental data allowing to understand how the uptake coefficient was measured and to judge the quality of the experimental results are not presented in the manuscript. In the revised version the authors should detail the experimental approach used and particularly the following issues should be addressed:

(A1) In the revised manuscript, we have detailed the experimental approach used and the following issues (see below).

(Q2) to indicate how the contact time between  $\text{H}_2\text{O}_2$  and surface was calculated and if it was varied;

(A2) Figure 1 in the revised manuscript shows the schematic diagram of the experimental set-up that consists of three main parts: reactor, pumping and gas handling system, and  $\text{H}_2\text{O}_2$  detection system. The reactor (length 15 cm, ID 3.3 cm) is a quartz tube with two infrared windows made of ZnSe. The  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{CaCO}_3$  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  $0.86 \text{ cm s}^{-1}$ ). 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.

(Q3) to give an example of  $\text{H}_2\text{O}_2$  consumption kinetics; to show original data from which uptake coefficient was determined; to show the experimental data on the dependence of the uptake coefficient on exposure time of the surface to  $\text{H}_2\text{O}_2$  and to specify

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which value of the uptake coefficient was really measured: the question is if the steady state for the uptake coefficient really exists and even if so, the timescale of the surface deactivation can be different under different RH and surface coatings;

(A3) In the present study, the loss of gas-phase  $\text{H}_2\text{O}_2$  was measured as  $\text{H}_2\text{O}_2$ -containing airflow exited the reactor. Two kinds of measurements were carried out: one was in the presence of particles (to get total loss of gas-phase  $\text{H}_2\text{O}_2$ ) and one in the absence of particles (to obtain the wall loss of  $\text{H}_2\text{O}_2$ ). Figure 2 in the revised manuscript shows an example of  $\text{H}_2\text{O}_2$  uptake kinetics by alumina particles at 45% RH and surface nitrate coverage of  $3.4 \times 10^{18}$  molecules  $\text{m}^{-2}$ . Some loss (less than 5%) of gas-phase  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$ , the uptake of  $\text{H}_2\text{O}_2$  by mineral particles can be derived. It can be seen that at the initial exposure stage, the uptake of  $\text{H}_2\text{O}_2$  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. Similar phenomenon was observed for  $\text{H}_2\text{O}_2$  uptake kinetics under other conditions (different RH and surface coating).

In this study, the uptake coefficients of  $\text{H}_2\text{O}_2$  on processed particles were calculated using eqs (1) and (2) (see the revised manuscript). The uptake rate ( $d\{C\}/dt$ ) of  $\text{H}_2\text{O}_2$  was determined from the linear fit to the time-dependent uptake data within the first 10 min of exposure. It should be noted that although the timescale of the surface deactivation is different under different RH and surface coverage of coatings, a linear dependence of  $\text{H}_2\text{O}_2$  uptake could be still observed with the first 10 min of exposure. However, the  $\text{H}_2\text{O}_2$  uptake experiments in this work were performed at relative high  $\text{H}_2\text{O}_2$  pressures, and on the timescale of several minutes the initial uptake processes may have already been achieved. Therefore, we think the measured uptake coefficients here may represent steady state but rather the initial state.

(Q4) to make and report error analysis on the measurements of the uptake coefficient.

(A4) In the present study, at least three individual experiments were averaged to get  $\text{H}_2\text{O}_2$  uptake coefficients under each experimental condition. Errors are given as  $\pm 1\sigma$ , where  $\sigma$  is the standard deviation for individual measurements. The errors are mainly related to the repeatability of the surface coverage coating, stability of  $\text{H}_2\text{O}_2$  gas-phase concentration, and accuracy of RH measurements.

The processing of mineral particles was performed independently in each experiment prior to  $\text{H}_2\text{O}_2$  uptake, and the surface coverage coating is monitored using FTIR and determined using IC. The repeatability of the coverage for repeated experiments is within 10% on alumina and within 5% on  $\text{CaCO}_3$ . The concentration of gas-phase  $\text{H}_2\text{O}_2$  was measured before and after each experiment and it remained constant to within 5% over the time of a kinetic run. The RH in airflow was measured at the outlet of the reactor using a commercial hygrometer (Vaisala HMT100) with an accuracy of  $\pm 1.7\%$ .

(Q5) All these points concerning the measurements of the uptake coefficient are very important, especially when considering that all the effects observed in this study are relatively weak, not well pronounced. For example, all the data obtained for  $\text{HNO}_3$  treated surfaces under different RH and with different surface coverage (Figure 3) can be described as  $(0.8 \pm 0.3) \times 10^{-7}$ , i.e. are similar within 35% uncertainty, which is realistic for this kind of measurements. Considering that the observed effects are rather weak, the experiments with higher (than 15% and 6%, respectively) coverage of nitrate and sulfite would be very useful to confirm the observed trends. Additional experiments with varied concentration of  $\text{H}_2\text{O}_2$  would also be desirable.

(A5) It is reported that alumina is reactive insoluble and its reaction with  $\text{HNO}_3$  is limited to the particle surface. Thus, the coverage of nitrate on  $\text{HNO}_3$  treated alumina surfaces can not be very high, leading to a relatively weak effects on  $\text{H}_2\text{O}_2$  uptake. Compared to alumina particles,  $\text{CaCO}_3$  (calcite), as an important Ca-containing mineral dust in the atmosphere, is reactive soluble and especially reactive toward nitrogen oxides (Usher et al., 2003; Crowley et al., 2010). A number of field studies have observed a strong

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correlation between dust nitrate and  $\text{Ca}^{2+}$  (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  $\text{Ca}(\text{NO}_3)_2$  coatings mainly through the reaction with  $\text{HNO}_3$  (Kruegera et al., 2004; Li et al., 2009). Thus, the processed  $\text{CaCO}_3$  appears to better represent the atmospheric mineral dust aged by reaction with  $\text{HNO}_3$ . In view of this, in the revised manuscript we have performed a number of additional experiments on  $\text{HNO}_3$  treated  $\text{CaCO}_3$  particles with varying coverage of nitrate (1–10 monolayer), as well as on  $\text{SO}_2$  treated  $\text{CaCO}_3$  surface with sulfite coverage of 50% monolayer, and we have observed far more pronounced effects on processed  $\text{CaCO}_3$  particles (see details below). Besides, Additional experiments with varying concentration of  $\text{H}_2\text{O}_2$  have also been conducted (also see details below). The results suggest that the uptake coefficients of  $\text{H}_2\text{O}_2$  on  $\text{HNO}_3$  and  $\text{SO}_2$ -processed particles appear to be independent of  $\text{H}_2\text{O}_2$  concentration. This implies that the uptake behaviors of the processed mineral particles may be also applicable to lower  $\text{H}_2\text{O}_2$  concentrations.

The results and discussion of  $\text{H}_2\text{O}_2$  uptake on  $\text{HNO}_3$  and  $\text{SO}_2$ -processed  $\text{CaCO}_3$  particles as well as  $\text{H}_2\text{O}_2$  uptake at varying concentration of  $\text{H}_2\text{O}_2$  have been added to the revised manuscript as seen in Sections 3.2.2, 3.3.2, and 3.4, and Fig. 6, Figs. 9 to 12.

(Q6) In conclusion, although the manuscript seems to provide a new and interesting information, in my opinion, the work cannot be published in its present form and needs significant revision and, probably, additional experiments.

(A6) Thanks for your suggestion. In the revised manuscript, we have conducted a number of additional  $\text{H}_2\text{O}_2$  uptake experiments including those on processed  $\text{CaCO}_3$  particles and at varying  $\text{H}_2\text{O}_2$  concentrations. Please see the details in (A5) 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.

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