Atmos. Chem. Phys. Discuss., 7, S994–S1008, 2007
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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ice nucleation of ammonia gas exposed montmorillonite mineral dust particles" *by* A. Salam et al.

A. Salam et al.

Received and published: 5 April 2007

Anonymous Referee #1

Referee's comment: General comments: The paper shows experimental evidence that montmorillonite aerosols exposed to ammonia gas can activate ice particles at lower relative humidity than without gas exposure. The experiments have been made with a continuous flow chamber and appear to be well performed. The paper deals with an important topic in atmospheric research, since cloud formation processes are not fully understood, but clouds are important in the climate change discussion. The paper is generally well written, but I had some problems within the Results and Discussion part. I was several times lost with the numbers given in the text (see also specific comments). To my opinion, a table with the relevant numbers would help. Nevertheless, after the authors have addressed to the following points, I recommend the paper to be

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published in ACP.

Author response: *We thank the referee for the valuable and important comments to improve the quality of our manuscript. We have responded to all comments of the referee. We introduced two new tables into the manuscript that summarize the comparison between ammonia exposed and non-exposed montmorillonite dust particles and also the activation temperatures.*

Referee's comment: **Specific comments:**

Referee's comment: Page 384 lines 7-10: Enhanced to what? I guess to the unexposed case as written the next sentence.

Author response*: Yes, the referee is correct - the enhancement of the detected fraction of ice nuclei was compared with the unexposed case. We have changed the text by inserting "compared to unexposed montmorillonite".*

Referee's comment: Page 384 lines 9-10: 90% and 100% RHw mean xx% and yy% RHi, respectively? Give these numbers in brackets.

Author response: *We have mentioned 90% and 100% RHw in the abstract and also in the conclusions because these two values are fixed, but the corresponding values for the relative humidity with respect to ice are different as the experimental temperatures are different (-15, -20, -25, -30, and -35°C). Now it will be easier to understand as we have introduced the following table with the values of the relative humidity with respect to ice (RHi).*

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Table 1: Enhancement of ice nucleation due to the exposure of montmorillonite mineral dust particles to 100% pure and 25 ppm ammonia at 90% and 100% relative humidity with respect water (RHw) at different temperatures.

Temperature (^{o}C)	Corresponding relative humidity with respect to ice (RHi) in percentage (%)		Enhancement factor for ice nucleation (aged montmorillonite/ non aged montmorillonite)			
	For		100% pure NH_3		25ppm NH_3	
	100% RHw	90% RHw	100% RHw	90% RHw	100% RHw	90%RHw
-15	116	104	5	3	2	2
-20	122	110	8	5	4	3
-25	128	115	8	6	5	4
-30	136	121	8	5	-	-
-35	143	127	8	8	7	8

Referee's comment: Page 385 lines 8-10: Can you assign which mode belongs to the which experiment?

Author response: *We could not distinguish between condensation or deposition ice nucleation mode. We have carried out the ice nucleation experiments up to 100% RHw. However, there is a possibility of the condensation freezing mode for the ice nucleation especially at 100% RHw. We have changed the text as "**This paper presents experimental results where the ice nucleation occurs either in the deposition or condensation freezing mode".***

Referee's comment: Page 389 line 23: What about a lower limit of the nucleation rate?

Author response: *We have already explained into the text of the manuscript in section 2.7 that we are not able to calculate the nucleation rate.*

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Referee's comment: Page 392 lines 5-7: Do the authors rule out the condensation mode for the particles exposed with 25 ppm at 100% RHw, because the values 90% RHw reaches almost the same magnitude than that for 100% RHw? (Figure 4, bottom). The authors claimed that for pure ammonia exposure, the condensation mode is possible. Can I therefore conclude that the increase in the ammonia concentration could lead to a different nucleation mode?

Author response: *No. We could not rule out the possibility of the condensation mode at 100% RHw for the montmorillonite particles exposed to 25ppm ammonia. The magnitude of the values for 90% RHw and 100% RHw are not same (about 2 to 5 times higher at 100% RHw than 90% RHw depending on the exposure times).*

We are expecting mainly deposition nucleation, but at 100% RHw we can not rule out the possibility of condensation nucleation either for the non-exposed or the ammonia exposed montmorillonite mineral dust particles. With the increase of the ammonia concentrations on the montmorillonite surface - it may be possible that the montmorillonite particles undergo condensation freezing due to the water affinity of the ammonia molecule.

Referee's comment: Page 392 lines 7-9: How large will this underestimation be maximal? This could be crucial for the atmospheric adaptation of the experiments.

Author response: *Yes, we mentioned in the text that the percentage of the detected fraction of ice nuclei was underestimated since we are unable to detect the ice crystal $<5\mu m$. Unfortunately, we are unable to quantify this uncertainty.*

Referee's comment: Page 392 lines 17-20: It is not obvious to me how the authors have obtained these numbers. Why 3 to 8 times or 5 to 8 times? Two possible explanations may be reasonable to my view: 1) If one just compares the pairs of data points given in figure 5 (e.g., solid diamonds at -15_C and -35_C), one would end up in 1 number. For the case mentioned in the brackets, I would guess an increase in the activated fraction of about 4. Have you compared the minimal and maximal values of all

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series with each other, and thus a minimal and maximal increase are given? 2) Is just a “when compared to the unexposed particles" missing? If the authors do ever refer to other numbers than shown in one of the figures, a table with the relevant numbers would be extremely helpful.

Author response: *We calculated these number (enhancement of the detected fraction of ice nuclei) by dividing the average number of ice crystals of the 100% pure ammonia exposed montmorillonite with that of non exposed montmorillonite. The duration of each experiment was 60 seconds. The average ice crystal number concentration <5 μm was obtained from the average of 15 measurements at each temperature. We have introduced a table (Table 1) into the manuscript that will make it easier to understand the values.*

Referee’s comment: Page 393 line 3: Where in Figure 5 are the points for the experiments with 25 ppm performed at -30_C and -35_C?

Author response: *It was a mistake. We have inserted a new figure 5 with the data point at temperature -35°C for 25 ppm ammonia exposed montmorillonite. Unfortunately we do not have any experimental points at -30°C for 25 ppm ammonia exposed montmorillonite.*

Referee’s comment: Page 393 lines 10-13: See comment Page 392 line 17/20

Author response: *Answered above*

Referee’s comment: Page 393 lines 15-20: I don not understand the explanation to overcome the discrepancy with the previous studies. Birstein investigated silver iodide. Which IN did Georgh 1963 use in his experiments? You compare different IN, and thus one can conclude that the gas concentration is the determining factor, ant not the nature of the IN?

Author response: *We have deleted these sentences from the manuscript.*

Referee’s comment: Page 393 lines 23-26: The authors wrote The activation tem-

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perature of 25 ppm ammonia exposed montmorillonite mineral dust aerosols was -8_C at 100% RHw (108% RHi) (Fig. 5); whereas the activation temperature of unexposed montmorillonite was -15_C at 109%. Why -8_C? Figure 5 shows no data point at -8_C. This number obviously determines the difference of 7_C. Where does this number come from?

Author response: *We have calculated the activation temperature based on the definition of Salam et al 2006: "**Activation temperature is defined as the warmest temperature at which the detected fraction of ice crystals larger than 5 μm is at least 1% of the average of the total number of montmorillonite aerosol particles smaller than 5 μm before and after each ice nucleation experiment. This activation temperature criterion is tightly related to our experimental setup and care should be exercised when comparing it with other studies."** We also introduced a new table with the activation temperatures into the manuscript:*

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Table 2: The activation temperature of pure (100%) ammonia exposed montmorillonite, 25 ppm ammonia exposed montmorillonite, and non-exposed (pure) montmorillonite mineral dust particles at 100% and 90% relative humidity with respect to water (RHw).

Montmorillonite mineral dust aerosol particles	**Activation temperature (°C) at**	
	100% RHw	**90% RHw**
100% ammonia exposed	**-5**	**-15**
25 ppm ammonia exposed	**-15**	**-20**
Non exposed (pure)	**-20**	**-30**

Referee's comment: Page 395 lines 8-10: See comment Page 392 line 17/20;

Author response: *Answered above*

Referee's comment: Page 395 lines 12-13: How did the authors obtain the two numbers 10_C and 12_C?

Author response: *Now these values have changed (due to the calculation with a modified definition of activation temperature of 1% activated particles). The activation temperature of 100% pure ammonia aged montmorillonite mineral dust particles was 15°C warmer than that of the non-aged montmorillonite at both 100% and 90% RHw (Table 2).*

Referee's comment: Page 395 line 19: The authors make the following statement: "This is the first experimental evidence for an enhancement of ice nucleation by mineral dust aerosols exposed to ammonia gas. Although the ammonia concentrations used are higher than those found in the polluted atmosphere the effect has been demonstrated and future experiments will be performed using lower concentrations." The at-

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mospheric NH3 concentrations are 3 orders of magnitude smaller than in this study. Is it possible that the ice nucleation enhancement is negligible small under atmospheric concentration? Is it likely that a threshold concentration must be exceeding before any enhancement takes place? I would like to see a more detailed discussion, because the NH3 concentration seems to be crucial for the observed enhancement. Can the authors be certain that the low ammonia concentration in the atmosphere do still result in a distinct ice nucleation enhancement?

Author response: *We agree with the referee's caution about what might be happening at actual atmospheric ammonia concentrations. We were careful in our wording throughout the manuscript to avoid any impression that our experimental conditions occur in the atmosphere. Indeed we already pointed out that atmospheric ammonia concentrations are much lower. However we have discovered a new nucleating influence at 25 ppm which we feel is important to report on. It would be complete speculation in trying to extrapolate to 25 ppb, so we decided to avoid that and instead we are currently working at producing lower concentrations in future experiments.*

Referee's comment: Page 403 Figure 5 shows that particles exposed to 100% ammonia gas at 100% RHw may activate about 2.5% of the total particle at temperature larger than -10_C. What about the experimental uncertainty in detecting the percentage of activated particles? The included standard deviation for some data sets just indicates the reproducibility of the measurements? The reproducibility for the two filled squares at -5 and -10_C is less than the size of the symbol?

Author response: *Yes the error bars shown are the standard derivations which are determined from the reproducibility as stated in the figure caption. The reproducibility also includes random variations in the detection of activated particles in the way we have defined activation. Since particles less than 5 μm are not included we likely have a systematic underestimation of the actual nucleation rate as discussed in the manuscript.*

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Referee's comment: Technical corrections:

Referee's comment: Page 385 line 2: Does the Knopf and Koop 2006 paper deal with radioactive properties of clouds?

Author response: *We have deleted this reference from the text and also from the reference list*

Referee's comment: Page 385 line 8: "...above -20_C". A citation would here be desirable.

Author response: *Done*

Referee's comment: Page 385 line 20: Does the study of Möhler et al with montmorillonite? I thought they investigated Sahara, Asian and Arizona Test Dust.

Author response: *Yes, the reviewer is right. We have changed the text accordingly.*

Referee's comment: Page 386 line 11: Put "45 cm ... 20cm" into brackets

Author response: *Done*

Referee's comment: Page 392 line 25: -27_C? I can not see any data point in Fig 5 at this temperature.

Author response: *This value has changed now and the new value is -20°C (Table 2 and Figure 5). From the definition of activation temperature (1% activated particles) we have calculated the activation temperature, and found that the non-exposed montmorillonite particles were activated at -20°C at 100% RHw (Table 2).*

Referee's comment: Figures: Use equally steps for the numbers on the x-axis in Figures 2 and 3. Minor ticks on the y-axis of figures 2, 4 and 5 would be helpful.

Author response: *We have changed the x-axes of figures 2 and 3 and also inserted minor ticks in the y-axes of figures 2, 4 and 5; and we also introduced the relative humidity with respect to ice (RHi in %) in the legend of figure 4.*

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Anonymous Referee #2

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Referee's comment: **General comments:** This paper investigates the effect of ammonia exposure on the heterogeneous ice nucleation by montmorillonite particles. The dust samples were exposed to either pure ammonia gas or a volume fraction of 30 ppmv in nitrogen at variable time periods. The ice nucleation induced by particles of diameters as large as 5μm, which were dispersed from the montmorillonite samples by a vibrating membrane technique, was measured with a new continuous flow diffusion chamber (CFDC) instrument at temperatures between -5 and -35^{O}C and two distinct relative humidities of 90 % and 100 % with respect to liquid water. Despite the fact that, as carefully mentioned in the manuscript, atmospheric dust particles are typically exposed to much lower ammonia concentration compared to the laboratory procedures, the work presented in the manuscript by Salam et al. is an important and relevant piece of information of how the ice nucleation of mineral particles depends on their surface characteristics. In addition to the different concentrations and exposure times in the atmosphere and in the laboratory approaches, it should be noted here that in the atmosphere the majority of ammonia molecules interact with acids like sulphuric acid and nitric acid. Therefore, the effect of surface coatings with ammonium sulphate or ammonium nitrate or mixtures of those with organic substances should be more important in the atmosphere than pure ammonia exposure. On the other hand, I am somewhat concerned about the quality of the results at least in their presented form (see my list of comments and questions below). This is mainly related to the poor and incomplete description of the experimental methods and to the fact, that actually only a lower fraction of the nucleated ice particles are detected (those larger than 5μm in diamter), but in the text and also the Figures the results are presented as 'active ice fraction' of the aerosol. Of course a lower limit of ice activity is still a conservative estimate and important result, but some of the conclusions concerning the dependence

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on temperature and the relative humidity may be affected by the fact that the fraction of undetected ice particles may vary with these parameters. After an extension of the experimental part and revisions outlined below the paper may be accepted for publication in ACP.

Author response: *We thank the referee for the constructive comments, which will greatly improve the quality of the manuscript. We have introduced a detailed description of the particle counters in the experimental part of the manuscript. We used an aerodynamic particle sizer (APS), TSI 3321 for the characterization of the size distributions of the montmorillonite mineral dust particles after the impactor and before the CFDC chamber (Figure 2). The APS was also used to verify the accuracy of the MetOne optical particle counter. The MetOne optical particle counter was used for measuring the ice crystal number concentration at the outlet of chamber. According to the referee's suggestion – the y-axes of figure 4 and 5 has been replaced by the detected fraction of ice nuclei (%).*

Referee's comment: Major Questions and comments:

Referee's comment: Does Figure 2 show the size distribution measured before or after the impactor?

Author response: *Figure 2 shows the size distribution of montmorillonite mineral dust particles after the impactor system with a size cut off 5 μm. It shows the size distribution of montmorillonite mineral dust particles before and after exposure to ammonia. The current CFDC system does not allow measuring the size distributions before and after the impactor.*

Referee's comment: At the end of section 2.4 you state that 'only montmorillonite particles smaller than 5 μm enter the CFDC'. However, an impactor normally is characterised with an S-shaped cut-off curve of a certain width. What was the cut-off diameter of the impactor. Did you measure the characteristics of the impactor? Did really no particle larger than 5 μm enter the CFDC?

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Author response: *Yes, the statement at the end of section 2.4 – "'only montmorillonite particles smaller than 5 μm enter the CFDC" is true (one can see that from figure 2). We have given the detail description of the impactor construction and design and its characteristics in Salam et al 2006 in Aerosol Science and Technology. The design of the impactor is not new - we have designed and built our impactor on the basis of Marple and Willeke, 1976 and Rogers et al., 2001. The cutoff diameter of this impactor system is 5 μm. Yes, we measured the characteristics of the impactor. Yes, about 0.03% particles larger than 5 μm enter into the CFDC flow, which is in the noise level as shown in figure 2.*

Referee's comment: If the OPC measures particles larger than 0.3 μm as mentioned in section 2.6, the instrument should also detect all the dust particles shown in the size distribution of Figure 2. I note that the MetOne OPC had only 6 size bins and therefore provide only a poor size resolution, but at least the total number counts of the APS and the OPC should compare to each other. Why was the number counts in the larger (ice) size bins not just related to the counts in the smaller size bins? What are the bin edge sizes of the OPC? If particles are counted in only 6 size bins, could a slight shift of the bin sizes, e.g. by slight changes of the refractive index due to variable amounts of water attached to the particle surface, have affected the number counts in the smallest size bin interpreted as only ice bins. How many size bins have been used for the ice detection and how have the number counts been distributed in these bins?

Author response: *The APS is used for the size distribution of montmorillonite mineral dust particles in figure 2. We measured the total number concentration of mineral dust particles with both the MetOne and APS for the comparison. We found their results (variation of the number concentrations) to agree within 5% for the same size range.*

The MetOne particle counter has 0.3, 0.5, 0.7, 1.0, 2.0 and 5.0 μm size bin limits. For the ice crystal number concentrations we used only the $>$5.0 μm size bin. The range for 5.0 μm size bin is 5.0–20 μm. We are unable to say where within the 5 to 20 μm size range most of the ice particles reside.

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We ruled out the possibility that variable amounts of water attached to the particle results in a false ice particle count by performing experiments at 100% RHw at -2°C and found no enhancement of particles greater than 5 μm. Under these conditions the swelling of the particles due to water uptake would be the greatest, but it did not result in particles greater than 5 μm. A description about the hygroscopic growth of the montmorillonite in the manuscript is given in section 3.7.

Referee's comment: Can you estimate the fraction of ice crystals smaller than 5 μm that could not be detected in the experimental setup? What about the aerosol particles with aerodynamic diameters smaller than about 0.5 μm. Have they been disregarded in the calculation of the activated fraction? The fact that the results give a lower limit of the activated fraction should be more clearly stated in the manuscript (e.g. replace 'Active ice nuclei' in Figures 3 and 4 by something like 'Detected fraction of ice nuclei') should more clearly be stated in the manuscript and the potential systematic errors like missing ice crystals or incomplete size distributions (if relevant) should be estimated, if possible. What do you mean with 'The noise level was determined from particle artifacts measured during the blank and dry experiments'?

Author response: *We have introduced a discussion about the limitation for the determination of ice crystals number concentration. Due to this limitation for the smaller particles we are forced to consider only the ice crystal number concentrations larger than 5 μm.*

We agree with the referee's comment. According to his suggestion we have replaced "Active Ice Nuclei" in Figures 4 and 5 by "Detected fraction of ice nuclei".

The noise level is determined from the average of the dry and blank experiments for the particles larger than 5 μm. The average value is then inserted into the figure 2 as noise level. Blank experiments are those with no aerosol input into the chamber, but the walls of the CFDC chamber were covered with ice. Dry experiments have no ice coating on the CFDC walls but montmorillonite particles were allowed to enter into the

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chamber. We have introduced a description for the blank and dry experiments, and also a description for the determination of noise level in the manuscript.

Referee's comment: The quality of the Figures should be improved. In Figure 1, the lines are rather thick and the font size is small. Thinner lines and larger font would certainly improve the readability of the figure. Is there any reason for the uneven numbers at the x-axis of Figures 2 and 3? Tick marks are missing in Figure 3. To show the dependency of the ice nucleation on exposure time, a respective time scale (linear or log) should be used instead of the equally distant plot format on the x-axis. Otherwise use a bar chart format.

Author response: *We have changed figure 1 with thinner lines and lager font according to the referee's comment. We have changed the x-axes of figures 2 and 3 to even numbers, inserted tick marks x-axis in the figure 3 and also inserted minor ticks in the y-axes of figures 2, 4 and 5. A linear scale has been inserted in the figure 4 to show the time dependence on the detected fraction of ice nuclei (%).*

Referee's comment: How did you define the noise level in Figure 2?

Author response: *We determined the average of the dry and blank measurements for the particles larger than 5 μm and inserted that value into the figure 2 as noise level.*

Referee's comment: The description of the aerosol measurements with the APS and the optical particle counter (OPC) should be extended in the experimental section of the manuscript.

Author response: *In section 2.6 Detection of Ice Crystals: we have added a more elaborate discussion regarding the measurements of ice crystal with the MetOne optical particles counter. We also added a discussion regarding aerodynamic particle sizer (APS) in section 3.1.*

Referee's comment: **Minor comments and typos:**

Referee's comment: *p.385, l.27:* ...the interaction of...was investigated . . .

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Author response: *Done*

Referee's comment: *p.391, l.9:* ...which is absent in Fig. 3a: If you look closely the band at 3220 cm-1 also weakly appears in Fig. 3a. Any explanation for that?

Author response: *Yes the referee is right. There is a very weak peak at 3220 cm^{-1} in the case of pure montmorillonite (Figure 3a). Hydroxyl and amino groups show characteristic absorption bands (Coates, 2000; Ogloza and Malhotra, 1989) in the region from 3650 to 3200 cm^{-1}. Therefore the weak peak at 3220 cm^{-1} in the case of pure montmorillonite (Figure 3a) is most likely an extended peak of the hydroxyl groups. In figure 3b and 3c, the N-H stretching of the ammonia molecule result in a more pronounced peak at 3220 cm^{-1}. We added this statement in the text.*

Referee's comment: *p.391, l.13:* There is another small IR signature... Which one do you mean here?

Author response: *The peak is at 1420 cm^{-1} (it is already mentioned in the text).*

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 383, 2007.