

Interactive comment on “Surface modification of mineral dust particles by sulphuric acid processing: implications for CCN and IN abilities” by P. Reitz et al.

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We thank the referee for appreciating this work and for his constructive comments, especially concerning the readability of the manuscript.

Answers to general comments

1) Section 2.2.3, addressing details of the AMS measurements and necessary correction factors, is hard to read for a non-expert in AMS measurements. On page 7243, line 22ff, the authors introduce which information is contained in the following paragraphs, but I would definitely suggest to split the following information into further subsections

C5213

like “Correction for the collection efficiency”, “Correction for the lens transmission” etc. On page 7244, line 1, the first sentence addresses the instrument calibration but the next sentence then already addresses the collection efficiency. The AMS calibration is then again referred to later on page 7246, line 17. These two parts should be grouped together.

I did not really understand how the comparability factors shown in Table 2 were derived. Concerning the statement on page 7246, line 10: Why do you refer to the CCNC measurements in this context? Are they also affected by the dilution stage? The comparability factors imply that there is a 4 - 5 times difference in the uncorrected AMS data for the same experimental conditions between FROST 1 and 2. How does this compare to the assumed uncertainty of only 10% for the dilution stage? What are the other speculative sources mentioned in line 5?

The authors agree that the technical details in the correction factor section are hard to follow for non-AMS experts. They will therefore be moved to the appendix section. Within the appendix, we then use the proposed subdivision to improve readability.

The difference in detection efficiency between the two campaigns can not be completely explained. We do not expect to have such high discrepancies between the campaigns and we did not observe such differences between other measurements using this instrument. We stated those influences that we understand. A possible reason could be a non-optimal alignment of the aerodynamic lens, such that not all particles hit the vaporiser. If this was the case, it must have occurred during the final set-up of the instrument, as the lens was adjusted prior to the campaigns. During the campaigns the mass per particle loadings for similar experimental settings were stable. Thus we can exclude any misalignment during the campaigns. In order to compare the two campaigns, which is necessary for the chemical analysis we effectively did a calibration of the AMS to the CCNC for all campaigns. There were three measurements performed: The FROST1 and FROST2 campaign, and one short third campaign that was only

C5214

meant to determine correction factors. We compared the mass per particle measured during the short third campaign to the mass per particle for the identical experiments performed during the main campaigns FROST1 and FROST2. The CCNC measurements showed excellent agreement between the main campaigns and the short third campaign. Thus scaling of the AMS data to the CCNC data is justified. It is important to notice that for every campaign only one correction factor was needed. The comparison between the CCNC and the AMS is thus still valid and an agreement is not forced by the calibration.

2) Section 3.1, discussion of Figs. 6a-c: The authors have obviously put the results from all individual FROST 1 and 2 experiments into the figures which makes them very difficult to read and to extract the major conclusions. A particularly bad example is Fig.6c which is only described by a few lines on page 7251 and also contains experiments (like the one labeled "lr" with the longer residence time) that are not discussed and explained in the manuscript text at all. I understand that the authors want to show all of the experiments – but then they could e.g. include an overview table which shows the experimental conditions of all experiments performed during FROST 1 and 2, and then simplify Figure 6c by just showing a set of examples (e.g. just one conditioning temperature) that underline the major conclusions that are described in the manuscript text. In the manuscript text itself, the authors should add more references to the experiments in the figures to which the current discussion is related to. For example, in the paragraph starting on page 7250, line 28, they presumably address the final experiment shown in Fig. 6a that shows the reduction in the sulphate mass. It would be much easier and a better guide for the reader if this were also announced in the text. Figure 6c e.g. contains too much information. Concerning the statement on page 7251, line23: The reader would more easily see this effect if only an exemplary set of experiments that underlines the subject under discussion would be shown.

The section addressing the mass per particle will be changed as follows using the new figures Fig. 1 - 3. The complete new captions of the figures are presented prior to the
C5215

figures for technical reasons:

In Fig. 1, the non-refractory mass per particle for uncoated and coated particles measured during the FROST1 campaign is shown. In FROST1, the vaporiser of the AMS was set to 600 °C. At this temperature we expect sulphuric acid, ammonium sulphate, organic compounds as well as silicone to evaporate. Carbonates, however, do not decompose efficiently. The left graph of Figure 1 shows that on uncoated ATD particles, the detected silicone and carbon containing matter (CCM) in mass per particle is approximately proportional to the square of the particle diameter and thus to the particle surface area. This implies that these substances are most likely surface contaminants of the ATD particles. On particles coated with sulphuric acid, the coating mass per particle increases with the square of the particle diameter (Fig 1, right graph) when the sulphuric acid bath is operated at 70 °C. For particles which were coated at a temperature of 50 °C the increase in sulphate is lower than the increase in surface area. It is possible that at lower H₂SO₄ bath temperatures (50 °C) not sufficient H₂SO₄ is released to the gas phase to coat larger particles with the same thickness as smaller particles. However, for the later evaluation this is not relevant.

Figure 2 shows the measured mass per particle values for 300 nm particles as a function of coating bath temperature. The left graph of Figure 2 shows the amount of coating material as a function of the coating bath temperature. As expected we find an increase of sulphate with increasing bath temperature. This increase is larger for 820 °C vaporiser temperature than for 600 °C, indicating that a certain amount of sulphate is not evaporated at 600 °C. Experiments with the thermodenuder in operation at 250 °C also indicate that a certain amount of the sulphate coating is not evaporated at 250 °C.

The right graph shows that CCM and silicone decreased, as both species react with sulphuric acid. Also for the 200 nm particles (not shown), the silicone signal is reduced to zero for 70 °C coating temperature and also shows a reduction at 45 and 50 °C. In contrast, CCM is not reduced at higher H₂SO₄ bath temperatures (Fig 2, right graph).

To study the influence of humidity and neutralisation by ammonia, particles were humidified after the coating and afterwards optionally exposed to an elevated ammonia gas concentration. The left graph of Figure 3 shows the sulphate mass per particle for these experiments with 300 nm particles for vaporiser temperatures of 600 °C and 820 °C.

Interestingly, the sulphate signal is clearly reduced after this processing for the lower vaporiser temperature, while it is increased for higher vaporiser temperatures. This indicates a reaction of H_2SO_4 with some particle components, forming a reaction product that cannot be evaporated by the AMS at 600 °C but at 820 °C. Further indication for such a reaction is the finding that silicon is not removed as effectively during these experiments than it is during the experiments without humidification. Thus, humidification appears to accelerate the reaction of H_2SO_4 with the surface components of the particle.

The right graph of Figure 3 shows the data for 820 °C and data where the thermodenuder was additionally applied at 250 °C. There is a reduction of the sulphate signal by 10 to 20 % for both data sets (with and without NH_3), but the decrease of the sulphate signal is by far smaller than in Fig. 2 (right graph) where the pure H_2SO_4 coating was treated by the thermodenuder. This is a further indication for the accelerated reaction by humidifying the coated particles, leading to the formation of a low-volatile product.

The addition of ammonia to the aerosol has no clear effect to any of the experiments. Nevertheless, for those experiments with the water bath in use, the amount of ammonium is increased. In the case of the experiments with a coating bath temperature of 85 °C, the experiments with water bath provided sufficient ammonia for neutralisation of about 50 % of the sulphuric acid. These two experiments are the only experiments for which the ammonium signal was high enough to be detected. With the thermodenuder, the ammonium signal is reduced by approximately a factor of four but can not be quantified anymore.

C5217

3) Section 3.2: Please only show a selection of experiments in Figs. 8a/b that underline the conclusions from the manuscript text (e.g. just show experiments for a single bath temperature in Fig. 8b). If you state in the manuscript text "this difference is clearly visible" (page 7252, line 7), please mention specific experiments in the figures where the reader can actually see this difference. In Fig. 8a, there is an experiment labeled > 300 for the particle mobility diameter which shows a huge signal of the HSO_3^+ ion although using the water bath. What is the difference to the left-hand counterpart? I really had problems to extract the key aspects from the discussion in this section (e.g. concerning the role of ammonia). There is just one long paragraph, first addressing the results from the fragmentation patterns in Figs. 8a/b, and then e.g. in line 13 on page 7252 - without any break - there is a statement that obviously refers to some experiments from Fig. 6c. As a reader, I also somehow felt like being left alone with the reaction schemes presented at the end of this chapter – I had to read again the previous discussion to reconstruct the proposed reactions. In my opinion, this could be much better arranged. The authors could, e.g., first introduce the reaction scheme and then explain step by step by addressing the observations from Figs. 6 and 8 why the proposed reactions are the most likely pathways. In a separate paragraph, e.g., the authors could summarise the key differences for the experiments with the water bath compared to those with the unprocessed SA coating, leading to the proposed reactions (R1) and (R2). In the next paragraph, the authors could address the "thermodenuder only" results and finally the water bath + thermodenuder experiments. Why is the the 250C thermodenuder reaction in line 10 doubly labeled (R6 and R7)?

We think that the data can be shown completely in one graph but with a new design (Fig. 4). It combines the suggested idea of a table with a graph. The graph showing the fragmentation during FROST1 (8a) was removed as it proved rather confusing than improving the understanding. The category with a diameter somewhat higher than 300 nm (>300) is only a single measurement and thus the effect of the higher HSO_3^+ signal might not be relevant. The effect of the reaction is much clearer in the Fig. 8b of the

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discussion paper, which is now the Fig. 4 in the response.

Figure 4 will be explained in the text as follows after the explanation of the fragmentation for sulphuric acid, ammonium sulphate and metal sulphates:

... Figure 4 shows the hydrogenated fragments for experiments with coated ATD after different treatments. The blue background refers to a sulphuric acid bath temperature of 45 °C, the green and the red background refer to coating temperatures of 70 °C and 85 °C, respectively. The categories on the right of the dashed line of each coating temperature correspond to measurements for which the water bath was used and/or the thermodenuder was used at a higher temperature as was used for the coating itself.

Comparing the categories on the left side of the dashed line for the different coating temperatures to those categories on the right shows that the use of the thermodenuder and/or the water bath reduces the hydrogenated fragments. This indicates that after these treatments, most of the sulphuric acid reacted with components on the particle surface to form metal sulphates, which no longer contained hydrogen atoms. At coating temperatures of 45 °C and 70 °C, the hydrogenated fragments disappeared nearly completely. However, for particles coated at 85 °C the hydrogenated fragment ions still have significant intensity. Possibly, the reaction with the particle surface was not fast enough for these thicker coatings to completely consume the sulphuric acid. Furthermore, the ammonium signal (not shown) indicated that for those particles which were not heated in the thermodenuder, part of the sulphuric acid reacted with ammonia to form ammonium sulphate and was therefore no longer available for reactions with the ATD surface.

The reaction scheme will be introduced earlier and split into three parts. The reactions are first introduced and explained afterwards for each of the processings. The figures will be referred to as suggested for every processing. The second label (R7) of reaction R6 will be removed.

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4) Section 3.4: Some general questions concerning the discussion: Can the authors estimate a coating thickness based on deduced mass per particle results? On page 7260, line 1, they state that only after humidification there is a highly concentrated sulphuric acid solution around the particle – does the humidification not lead to a reduction in the sulphuric acid concentration? What is the RH in the humidification section so to estimate the sulphuric acid concentration? For how long are the particles exposed to the increased RH? (residence time) Are there literature findings that show that less concentrated sulphuric acid solutions more easily react with carbonates etc.? And an important issue that is completely missing in the discussion: How do the applied particle treatments relate to processing that actually occurs in the atmosphere?

The coating thicknesses will be included. They can be calculated under the assumption of spherical particles of the given mobility diameters. For the particles of a mobility diameter of 300 nm and a coating bath temperature of 85°C, the thickness corresponds to ca. 6 nm. The statement that refers to the highly concentrated sulphuric acid solutions was meant to emphasise the fact that after humidification the particles were covered by a solution in contrast to pure sulphuric acid. The relative humidity in the humidification section was not measured, but it should have been close to 100% as the air passed over a water surface. The dissolution factors of the sulphuric acid can be estimated using Köhler theory, but the estimation is strongly dependent on the assumed relative humidity. If it was 100%, the dilution was, for the 6 nm coatings, approximately a factor of 1000. If the relative humidity was 90 %, the dilution would have been roughly a factor of 10. The residence time in the water bath section was approximately 70 s.

The main interest of this paper was to better understand the principle nature of mineral dust ice nuclei. The experiments are only of limited atmospheric relevance. However, the use of the water bath corresponds to smog processing of the ATD. If dust is suspended in a highly polluted region, unreacted sulphuric acid is present and can condense on the particle surface. If the relative humidity increases, these particles can grow hygroscopically and an effect similar to the water bath effect in these experiments

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is expected.

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Full figure captions

Fig. 1 Left: Non-refractory mass per particle for uncoated ATD particles as a function of particle diameter. Vaporiser temperature: 600 °C (FROST1). The quadratic fits forced through zero indicate that both CCM (carbon-containing material, left scale) and silicone (right scale) are contaminants on the surface of the ATD particles. Right: Sulphate coating (50 °C and 70 °C coating bath temperature) as a function of particle diameter. The quadratic fit forced through zero indicates that the coating mass per particle is proportional to the particle surface for a coating temperature of 70 °C.

Fig. 2 Left: Sulphate coating (mass per particle) as a function of the H₂SO₄ bath temperature, detected at 600 °C and 820 °C vaporiser temperature. The thermodenuder (TD) operated at 250 °C removes only part of the sulphate. Right: Silicone and carbon containing mass (CCM) on 300 nm ATD particles coated with sulphuric acid. AMS vaporiser temperature: 820 °C (FROST2). Silicone is efficiently destroyed by H₂SO₄ while a certain amount of CCM remains on the particle.

Fig. 3 Left: Sulphate mass per particle for H₂SO₄ coatings with additional humidification (WB) and optional neutralisation by NH₃ detected at vaporiser temperatures of 600 °C and 820 °C. Right: Sulphate mass per particle for the 820 °C vaporiser data of the left graph, treated additionally by the thermodenuder (TD).

Fig. 4 Intensity of the fragments HSO₃⁺ ($m/z = 81$) and H₂SO₄⁺ ($m/z = 98$) normalised to the intensity of the fragment SO₂⁺ ($m/z = 64$) for the FROST2 campaign. On the horizontal axis, the first line now shows the thermodenuder temperature in contrast to Fig. 1, the second one indicates if the water bath was used, the third one if ammonium was added. The “lr” marked in the special line refers to an experiment with an additional residence volume of 10 L after the particle coating. The last line refers to the temperature of the sulphuric acid coating section.

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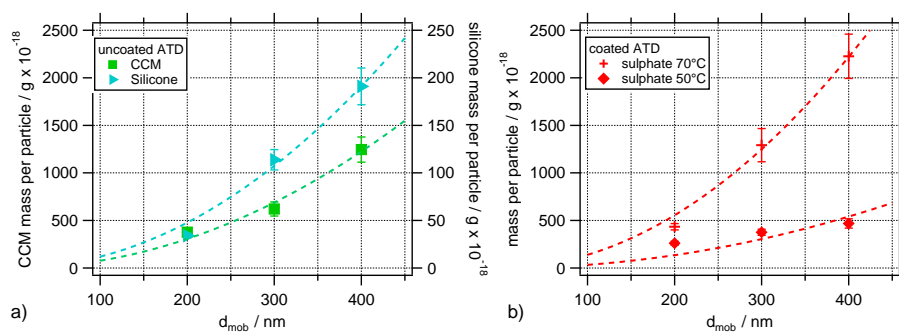


Fig. 1. Left: Non-refractory mass per particle for uncoated ATD particles as a function of particle diameter. Vaporiser temperature: 600 °C (FROST1). The quadratic fits forced through zero indicate that ...

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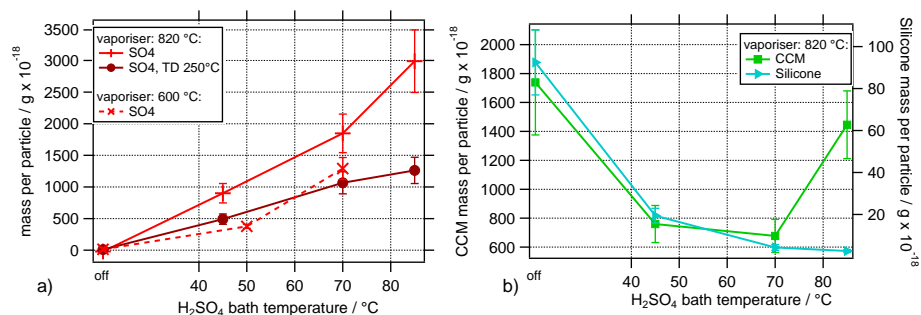


Fig. 2. Left: Sulphate coating (mass per particle) as a function of the H_2SO_4 bath temperature, detected at 600 $^{\circ}C$ and 820 $^{\circ}C$ vaporiser temperature. The thermodenuder (TD) operated at 250 $^{\circ}C$ removes only ...

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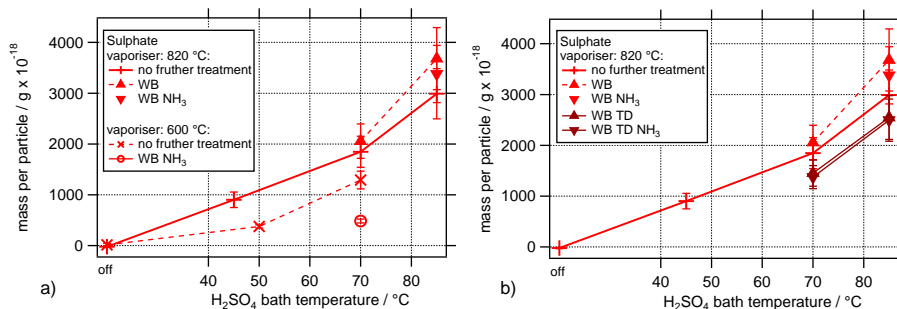


Fig. 3. Left: Sulphate mass per particle for H_2SO_4 coatings with additional humidification (WB) and optional neutralisation by NH_3 detected at vaporiser temperatures of 600 $^{\circ}C$ and 820 $^{\circ}C$. Right: Sulphate ...

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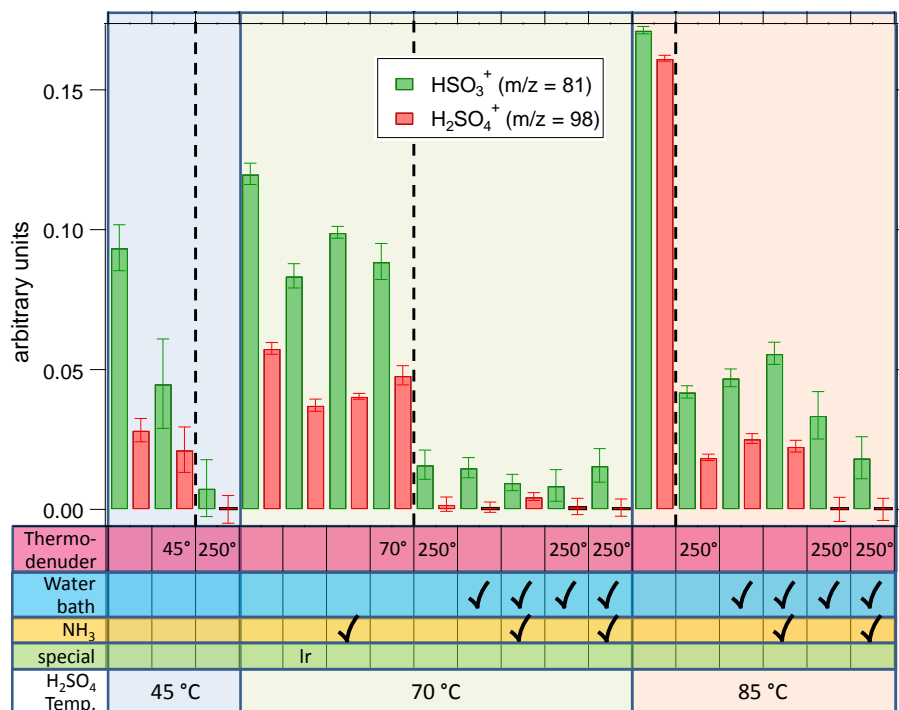


Fig. 4. Intensity of the fragments HSO_3^+ ($m/z = 81$) and H_2SO_4^+ ($m/z = 98$) normalised to the intensity of the fragment SO_2^+ ($m/z = 64$) for the FROST2 campaign. On the horizontal axis, the first line now ...