

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 would like to thank the referee for the comments and hints on how to improve the readability of the manuscript.

Answers to general comments

The manuscript entitled “Surface modification of mineral dust particle by sulphuric acid processing: implications for CCN and IN abilities” by Reitz et al. contains excellent information concerning the processing of mineral dust aerosols. With that being said, I found this manuscript very difficult to read and fully understand. There are a myriad of

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different experimental techniques used in this manuscript and there is much discussion about how to compare those techniques. Furthermore, there is much discussion about how to compare the two different experimental campaigns (FROST 1 and FROST 2). I feel like this manuscript should be drastically simplified which should not be too much of a problem since the manuscript is fairly long.

There is a significant discussion about the quantification of the amount of sulfuric acid on the particle surface using the AMS (Section 2.2.3). As an example of a simplification, perhaps the authors could present this section as a “supplemental section”. The correction factors could then be given in the text of the revised manuscript. This would knock out Figure 2, 3, 4 and Table 1. There is also significant discussion about the products formed from reactions on the surface of the dust particles (page 7254). The authors admit that they don’t know exactly which substances were created on the particle surface due to reactions. Therefore, as a second simplification, the authors could remove all discussion of possible reactions. They could then just focus on surface modification (and not on the specifics of the surface modification) which is important in the IN discussion later on.

Finally, the figures need to be worked on. The way the graphs were labeled made it very difficult to understand what all the numbers and letters meant. I was also unable to tell from the captions on the graphs, which particle size was being studied. Figures 6a-c and 8a had particle sizes labelled. The authors’ state that the particles most extensively studied had a mobility diameter of 300 nm. As a simplification, could the authors just focus on 1 particle size (e.g. 300 nm)? I would like the authors to comment on the ability to compare the data from FROST 1 and 2. Obviously, the authors are fairly confident that the two campaigns can be compared. However, with the amount of discussion about what it takes to compare the two campaigns, I am not so sure. Perhaps the authors should just focus on one of the campaigns or write two separate manuscripts describing each campaign. Focusing on one of the campaigns would help simplify the manuscript.

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The authors agree that the discussion about the necessary correction factors includes many technical details about the AMS which are difficult to understand for non AMS experts and impair the reading fluency. However, constraining the possible chemistry on the particle surface is only possible if a correct absolute determination of the mass per particle is achieved. Therefore the correction factors are an important part of this manuscript. To nevertheless improve the readability, we will put the determination of the correction factors into the appendix and not into the supplementary and provide more explanations to make them better understandable for those readers interested in the details.

The reason for the difference between the two campaigns is not quite clear. In fact, we do not expect to have such high discrepancies between two campaigns and we did also not observe such differences between other measurements using this instrument. What we effectively did when we determined the correction factors between the campaigns, is a calibration of the AMS to the soluble mass as detected by the CCNC for all campaigns. The calibration was performed for three cases: The FROST1 and FROST2 campaign, and one short third campaign that was only meant to determine correction factors. 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, which is more important. 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.

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We think the chemical analysis is important as it links surface modification to conceivable chemical processes. Therefore we do not want to remove the chemical analysis of the reactions taking place on the particle's surface and need both campaigns in this paper. We will however better explain the comparison factors in the appendix. The figures will be redesigned to improve their readability. Figure 8a will be removed, as it illustrates the same effect than Fig. 8b without adding to the understanding. Fig. 1 to 4 show the new design of the figures. The full new captions are presented prior to the figures for technical reasons. In the following, the new text for the section describing the mass per particle with the new figures is shown:

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

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°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 H₂SO₄ 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 H₂SO₄ 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 NH₃), but the decrease of the sulphate signal is by far smaller than in Fig. 2 (right graph) where the pure H₂SO₄ 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.

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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.

Description of Fig. 4 in the new text:

... 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

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ATD surface.

Technical corrections:

If nothing is mentioned the correction is accepted.

Page 7239, line 29 - artifacts

“artefacts” is the correct spelling in British English

Page 7243, Line 9 - should read “allowing further restriction of”

Page 7244, Line 15 - should read “thus they contained”

Page 7245, line 3 - I am not sure why the colon is there.

Page 7245, Line 9 - should read “S was determined to be approximately”

Page 7245, line 17 - “where” should be “were”

Page 7254, line 23 - (g) is not a good way to start a sentence. This was confusing.

Page 7254, line 25 - I am not sure why there is a colon after sulfur oxides.

Page 7258, line 2 - There is a huge space between the colon and the next word.

Page 7259 - line 3 - “two possible explanations”

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Figure 6a. I find the arrows in the caption (connecting the abbreviation in the figure with its description) confusing. There has to be a better way to do this. Figure removed.

Figure 6a - need to define WB in the caption

Figure 6c. This figure is almost unreadable. Something has to be done with the x-axis labels. There is almost no discussion of this figure in the text (lines 23-28 on page 7251). How am I supposed to know what “Ir” is and why it was done?

Figure removed.

Figure 7 - there should be a parenthesis after 98.

Figure 8a - There should be a °C after 50 in the second column.

Figure 8b - Again, the x-axis is nearly unreadable.

In this graph, the fragment SO_3^+ will be removed to reduce the information in the graph. The graph was also redesigned.

Figure 11. - “This graph was modified after Sullivan et al.” The word “modified” sounds strange here.

Maybe: “This graph is similar to the graph in Sullivan et al. with some modifications”

Figure 12. Should there be a “/” after 10-18 in the x-axis label?

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For the labels containing $\times 10^{-18}$, the factor will be put at end of the label like: "mass per particle / g/particle $\times 10^{-18}$ "

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 H_2SO_4 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 H_2SO_4 while a certain amount of CCM remains on the particle.

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 °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 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 shows the thermodenuder temperature in contrast to Fig. 1, the second one indicates if the water bath was used, the third one if ammonium

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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.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7235, 2011.

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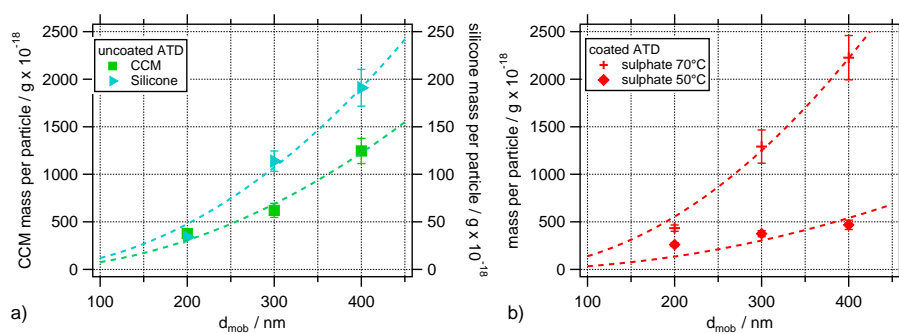


Fig. 1. Left: Non-refractory mass per particle for uncoated ATD particles as a function of particle diameter. Vaporiser temperature: 600 °C (FROST1). The quadratic fits forced through zero indicate that...

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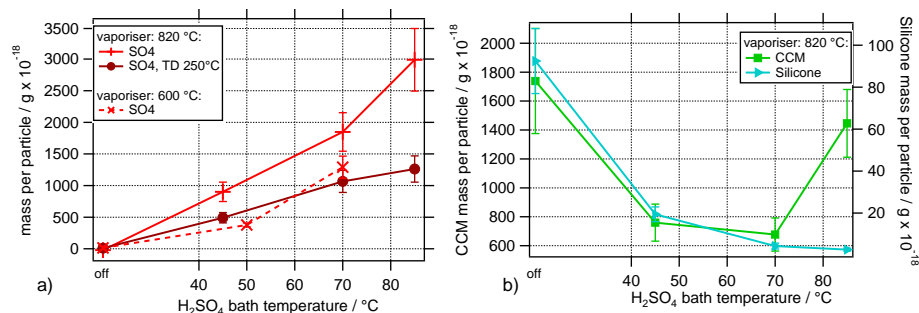


Fig. 2. Left: Sulphate coating (mass per particle) as a function of the H_2SO_4 bath temperature, detected at 600 °C and 820 °C vaporiser temperature. The thermodenuder (TD) operated at 250 °C removes only...

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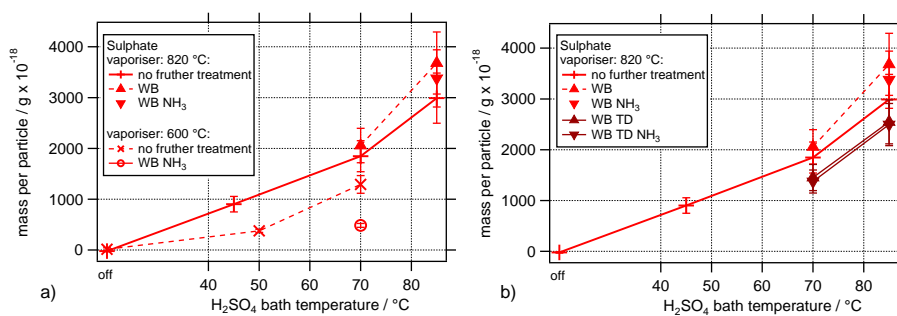


Fig. 3. Left: Sulphate mass per particle for H_2SO_4 coatings with additional humidification (WB) and optional neutralisation by NH_3 detected at vaporiser temperatures of 600 $^{\circ}\text{C}$ and 820 $^{\circ}\text{C}$. Right: Sulphate...

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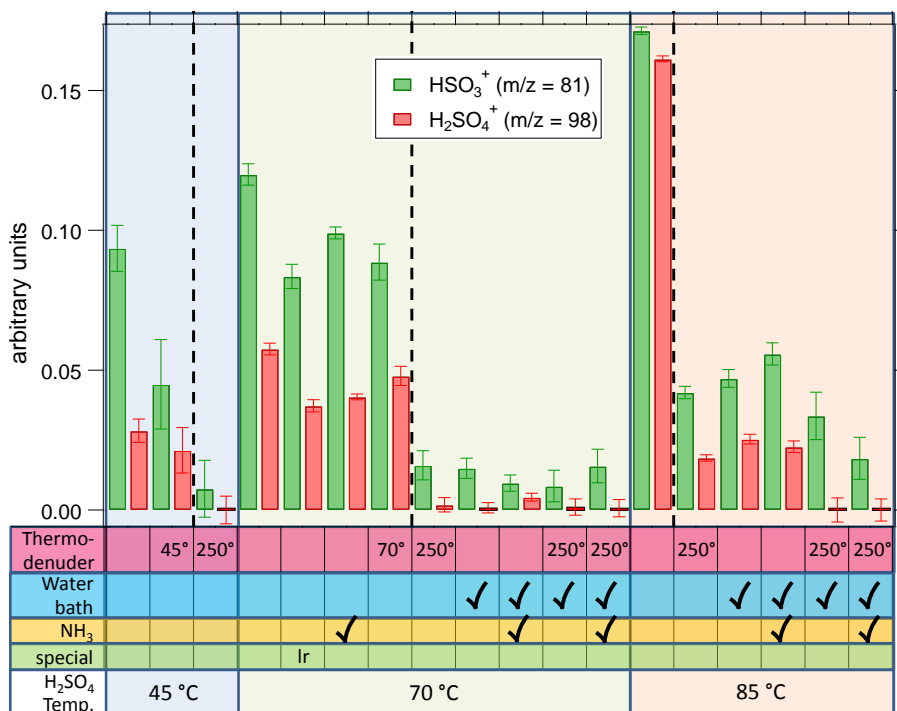


Fig. 4. Intensity of the fragments HSO_3^+ ($m/z = 81$) and H_2SO_4^+ ($m/z = 98$) normalised to the intensity of the fragment SO_2^+ ($m/z = 64$) for the FROST2 campaign. On the horizontal axis, the first line now...

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