

Interactive comment on “Effects of the physical state of tropospheric ammonium-sulfate-nitrate particles on global aerosol direct radiative forcing” by S. T. Martin et al.

S. T. Martin et al.

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We thank the reviewer for the time taken with our manuscript and the improvements offered.

Author responses are denoted below by *** response ***.

1. The authors find a substantial difference in radiative forcing depending on the physical state of the aerosol but consider a limiting - and quite unrealistic - hysteresis loop for their aerosol particles. If the relative humidity is below the DRH they take the composition of the lower side of the hysteresis loop from a thermodynamic model. But for some of the solid phases the efflorescence relative humidity (ERH) is so low that this solid phase will almost never form in the atmosphere. An example is ammonium nitrate for which it is known that the ERH is below a few percent at room

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temperature. For example the authors do not consider - and I agree completely - sulfuric acid tetrahydrate (SAT) as a possible solid in their calculations even though it is thermodynamically stable below circa 245 K. But it is also well known not to effloresce even under high supersaturations. Colberg et al. [ACP 3, 909-924 (2003)] have shown that ammonium bisulfate did not effloresce at typical tropospheric temperatures and the authors of the present paper have performed laboratory experiments for aerosol particles with the very composition discussed here [Martin et al., GRL 30, 2102, doi:10.1029/2003GL017930 (2003)] showing also that ammonium nitrate and ammonium bisulfate does not effloresce but at relative humidities so low that they will rarely occur in the troposphere. It is of course not easy to take this into account in the authors model, but since the ERH's of the system are known quite well [Martin et al., GRL 30, 2102, doi:10.1029/2003GL017930 (2003)] one could for example not allow ammonium nitrate and ammonium bisulfate formation and try to take a certain frequency of occurrences of relative humidities below 35% as a threshold where solid formation will happen. This will rule out entire regions/altitudes of the atmosphere for solid formation. (It is instructive to see Figure 5 and Figure 6 of Colberg et al. [ACP 3, 909-924 (2003)] in this context). I am convinced such a scenario - and the authors probably find a better one - could provide some information about how realistic the 25% delta forcing effect described above really is. Such sensitivity studies would nicely supplement what has been done by the authors in chapter 6 and increase the value of the paper considerably.

*** The reviewer's points are all well-taken. We would add the following points to this discussion:

1. As the reviewer states, ammonium nitrate and ammonium bisulfate do not form from aqueous solutions of the pure materials. However, our new laboratory results show that they do form from mixed solutions. For example, crystalline ammonium bisulfate forms in aqueous particles that are somewhat neutralized, i.e., an eight part mixture of ammonium bisulfate with two parts of ammonium sulfate. Letovicite forms first and then acts

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as a heterogeneous nucleus to crystallize ammonium bisulfate. Similarly, crystalline ammonium nitrate forms from aqueous particles that are eight parts ammonium nitrate and two parts ammonium sulfate. These experimental findings are new and modify the rule that has evolved over the last few years that crystalline ammonium nitrate and crystalline ammonium bisulfate do not form. We have a manuscript in preparation and presented the findings at the AAAR meeting in October 2003 in Anaheim, California.

2. Figure 2 of the manuscript makes the point that most of the changes in forcing arise from particles having compositions towards the ammonium sulfate pole. Ammonium bisulfate composition when treated by the thermodynamic model have only a very small contribution. In this sense, the importance of the discussion about whether these solutions form crystalline materials is decreased. To a lesser extent, the same can be said of ammonium nitrate. The crucial point is that the modeled atmospheric aerosol occurs largely in the pole of the ammonium sulfate composition, which overlaps the susceptibility region of radiative forcing (Figure 2). (This analysis omits the importance of $\text{NH}_4\text{NO}_3(\text{s})$ volatility.)

3. In the manuscript cited by the reviewer, which is Martin et al., GRL 30, 2102, doi:10.1029/2003GL017930 (2003), we presented the CRH humidities, but we did not identify the solids formed. In our manuscript under preparation, we report on those solids. When another solid such as letovicite forms, it is able to act as a heterogeneous nucleus to form crystalline ammonium bisulfate. Similarly, $(\text{NH}_4\text{NO}_3)_3(\text{NH}_4)_2\text{SO}_4$ acts as a heterogeneous nucleus for crystalline ammonium nitrate.

4. The reviewer's call for additional simulations is well placed. We are beginning this work now by improving the model so that on-line relative humidities will be available and particle phase can be modeled prognostically. We expect this project will lead to additional publications in the future.

With the reviewer's and our points taken together, we provide the following updates to the manuscript.

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Section 2.4.1 does already bring up some of these points: "The [X, Y] predictions are shown in Fig. 6 for each model grid box in the BL, MT, UT, and the entire troposphere. The locus of points for the entire troposphere overlaps 10 strongly with compositions having percent-delta-sigma > 0 (Fig. 2). The implication is that phase transitions strongly influence the optical properties of tropospheric particles. In the BL, where most aerosol mass resides, aerosol chemical compositions cluster towards the AS pole [1, 1]. The consequence is an increased impact for phase transitions on the optical properties of BL aerosol (cf. Figs. 2 and 6)."

To emphasize this very important point, we now repeat it in the conclusions section of the manuscript. On page 5434, we add: "The large magnitude of $\Delta F_{U,L}$ arises in large part because of the correlation in clustering towards the [1, 1] AS pole of both aerosol particle chemical composition (Figure 5a) and the susceptibility of the extinction coefficient to particle phase (Figure 2). Compared to the other solids, formation of AS is most important because it is thermodynamically stable at the highest RH values, where the US deviates most strongly from the LS of the hysteresis loop."

The other aspect we now clarify in a new paragraph in the conclusions is that there is uncertainty in the LS of the hysteresis behavior and that this uncertainty systematically decreases the predicted forcing. For example, if ammonium bisulfate does not form, then the LS loop considering ammonium sulfate, letovicite, and ammonium nitrate stays the same or shifts systemically upward throughout [X, Y] composition space (*) when compared to the LS loop of ammonium bisulfate, ammonium sulfate, letovicite, and ammonium nitrate. Even so, in the case of ammonium bisulfate, we expect the reduction between the contrast of LS and US behavior to be small because the formation of ammonium sulfate is key to the differential LS versus US optical depth (Figure 2). In contrast, ammonium nitrate is more important because if it does not form on the LS, its volatilization will be inhibited somewhat. Even in this case, however, the formation of crystalline ammonium sulfate will increase the ionic strength of the residual aqueous solution and drive ammonium nitrate volatilization, albeit to a lesser degree than if

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crystalline ammonium nitrate itself had formed.

(*The inset for [0.6, 0.6] in Figure 1c provides an example of the upward shift: if AHS does not form (solid 3), then the line for AN.AHS (solid 5) would continue. The result would be a decrease in the difference between US and LS for $RH < 29\%$.)

Specifically, we add to page 5434: "The number of solids included in the LS behavior directly influences forcing. At tropospheric temperatures, there are seven solids in the SNA system. However, according to laboratory studies, the crystallization of some of these solids such as AHS and AN occurs less readily than others such as AS and LET. ISORROPIA itself includes only four solids. On the one hand, if all seven solids crystallize, then the difference between the LS and US of the hysteresis loop increases, which suggests our $\Delta F_{U,L}$ values are lower limits. On the other hand, if fewer solids crystallize (say just LET and AS), then the difference between LS and US behavior decreases, which suggests our $\Delta F_{U,L}$ values are upper limits. This uncertainty notwithstanding, laboratory studies show AS crystallizes most readily of all the seven solids and, as mentioned above, Figures 2 and 5a together demonstrate that AS is the solid most strongly affecting the magnitude of $\Delta F_{U,L}$. The other important solid affecting $\Delta F_{U,L}$ is AN due to its volatilization. On the LS, if AS is allowed to crystallize but AN is not, then the increase in ionic strength of the residual aqueous liquid following AS crystallization still drives the partial volatilization of NH_3 and HNO_3 . We then conclude that our reported $\Delta F_{U,L}$ is a central value dependent mostly on AS crystallization and AN volatilization; consideration of the occurrence of other solids perturbs this central value."

2. The alternative approach - as e.g. done by Colberg et al. - namely taking into account directly the RH history of an air parcel, should be discussed more thoroughly by the authors, so that a reader not familiar with the specific field understands better that the present paper presents an upper limit of the effect of physical state on radiative forc-

ing. (The argument by the authors that it could also be a lower limit because not every solid thermodynamically conceivable is considered (see section 7) is rather weak, because these solid most likely never form in the atmosphere, see Martin et al. [GRL 30, 2102, doi:10.1029/2003GL017930 (2003)]). This comment is closely connected to the one raised already by J. Heintzenberg. Although the authors write three sentences in connection with their use of monthly average RH (and T) in section 7 the reader would appreciate a more detailed discussion.

*** On page 5404, we revise:

"Previous global modeling treatments of aerosol phase include: (a) prediction of phase but not direct radiative forcing and not including nitrate (Colberg et al., 2003)..."

to:

"Previous global modeling treatments of aerosol phase include: (a) prediction of phase accounting for the hysteresis effect using an RH trajectory analysis but not including nitrate in the aerosol chemical composition and not evaluating the effect of phase on global aerosol direct radiative forcing (Colberg et al., 2003)..."

The introduction does already state: "The major aim of our work is to compare the global aerosol direct radiative forcing FL and FU of SNA aerosol following the LS and US of the hysteresis loop." The reviewer's point is that we do not remind the reader enough of our goal to study the upper limit of effect of SNA phase transitions on forcing. Hence, on page 5435, we add to the paragraph: "Because the limiting scenarios of LS versus US behavior are calculated, we establish a central value for the upper limit of SNA aerosol on global aerosol direct radiative forcing. Given the significant differences we find between \$F_{US}\$ and \$F_{LS}\$, further global modeling employing prognostic treatments of aerosol phase to account for RH history is highly warranted..."

3. A further serious criticism - raised already by D. Cziczo - concerns the fact that

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organic material is excluded in the present study. I agree with Martin et al. that nevertheless the present study is important for improving our knowledge of how important physical state could be for aerosol radiative forcing. There is no alternative than proceeding in steps towards a more complex model, incorporating organics, elemental carbon inclusions, particles shapes and morphologies etc. (I want to stress again that a more realistic treatment for calculating the delta forcing would be very helpful). But I agree as well with D. Cziczo that the limitations of this study should be thoroughly discussed already in the introduction of the paper so that the reader not familiar with what is known about aerosol composition and the effect on aerosol phase get a better understanding. While the authors list the relevant studies in § 1.2 they should also explain and comment in more detail about the advantages and limitations.

*** The revised manuscript includes several new paragraphs on a description of the possible role of organic molecules. Please see the details in our second response to Dan Cziczo's comments. ***

4. Page 5403, line 6 and Figure 1: Since the authors use the ISORROPIA thermodynamic model with 4 possible solids, I recommend using the same model for Figure 1 for consistency and simply mentioning the additional solids incorporated in the AIM model.

*** We agree with the reviewer, and in our initial efforts for Figure 1 we tried to use the same models. However, the two models are interrogated differently. In AIM, gas phase partitioning can be turned off for all [X,Y] compositions. This is not possible in ISORROPIA. As a result, P(NH₃) and P(HNO₃) become so high over some [X, Y] regions that making a plot similar to Figure 1 from ISORROPIA is impossible. ***

5. Page 5403 and page 5404: Also it is known that (NH₄NO₃)₃ (NH₄)₂SO₄ is extremely difficult to nucleate even in bulk solutions [Jänecke et al., Z. anorganische und allg. Chemie 160, 171-184 (1927)]. It is likely that it is of no atmospheric relevance.

*** In our laboratory experiments with aerosol particles, we observe the formation of

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the mixed salts $(\text{NH}_4\text{NO}_3)_2(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4\text{NO}_3)_3(\text{NH}_4)_2\text{SO}_4$. We have a manuscript in preparation and presented the findings at the AAAR meeting in October 2003 in Anaheim, California. ***

6. Section 2.2: I recommend shortening it to what is absolutely essential for the present paper, see also comment by J. Heintzenberg.

*** We applied this maxim in writing section 2.2. We focused specifically on those elements crucial to our manuscript, viz. sulfate, nitrate, and ammonium distributions. Other aspects are covered in the Park et al. manuscript, which is now submitted and in peer review. ***

7. Page 5411, line 11: Some comment is needed here, because NH_4HSO_4 will probably not effloresce, see Colberg et al. and comment above.

*** We now clarify this aspect. Please see our reply to comment 1. ***

8. Section 3.1: Again the reader should be reminded at certain places (for example page 5415 line 3) that a solid whose formation is possible thermodynamically does not necessarily actually forms.

*** We now clarify this aspect. Please see our reply to comment 1. ***

9. Page 5417, line 16: The sentence is misleading. Figure 12 of Colberg et al. considers not homogeneous nucleation, but heterogeneous nucleation of the bisulfate. This should be explained to the reader. If only homogeneous nucleation would be considered in Colberg et al. there would be no agreement with the results presented here.

*** We add these sentences:

The special case analyzed in Fig. 12 of Colberg et al. (2003) is the assumption that LET acts a good heterogeneous nucleus for AHS formation. This particular assumption facilitates comparisons with our LS treatment. ***

10. Section 4 and 5: I find those very well written and instructive to the reader.

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*** Thank you ***

11. Page 5419, line 17: If besides the Bohren and Huffman citation another citation for optical properties and Mie theory is needed I would recommend citing the classic book of H. C. van de Hulst, Light Scattering by Small Particles, John Wiley & Sons, N. Y. 1957 instead of Han and Martin [2001] and Hung and Martin [2002].

*** The Hulst reference is added. We retained the Han and Martin and Hung and Martin references, too, because they provide examples of the specific algorithms used in this study. ***

12. Page 5420, line 3: A comment should be added to account for the vast literature of the effect an (soot) inclusion does have on scattering properties and radiative forcing, e.g. [Chýlek et al., JGR 100, 16,325 (1995), Ioannidou et al., Appl. Opt. 39, 4205 (2000)]

*** We added the following paragraphs:

Water insoluble organic inclusions inside sulfate particles influence aerosol direct radiative forcing. Especially important is black carbon (soot) because it absorbs solar radiation and contributes to atmospheric warming by aerosol particles (Jacobson, 2000). Due to a lens effect, the warming efficiency ($W\ m^{-2}\ (g\ C\ m^{-2})^{-1}$) increases when black carbon inclusions occur inside sulfate particles. A typical example is a 100 nm sulfate particle having a 40 nm black carbon inclusion. The additional warming typically partially offsets the cooling by sulfate, so the net effect is a less negative forcing.

For the purposes of this paper, we wish to assess how the relative warming efficiency of black carbon inclusions depends on the phase of the host particle. Figures 2a, 4a, and 5 of Lesins et al. (2002) are instructive. A base case is an externally mixed aerosol having 90% AS and 10% black carbon particles, in which the AS particles follow the US of the hysteresis loop. In comparison, when the aerosol particles are internally mixed, the single scattering albedo is 8% less for US behavior and 23% less for LS

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behavior at 80% RH (Figure 2a, Lesins et al., 2002). On the one hand, the darker LS particles favor increased warming. On the other hand, the scattering efficiency of LS particles is lower, which limits the amount of light absorbed and hence warming. The warming efficiency of black carbon is thus anticipated to depend on phase, although there are convoluted effects of a decrease in scattering efficiency with an increase in absorption. A radiative transfer model yields normalized aerosol direct radiative forcing of $G_L = -25 \text{ W g}^{-1}$ and $G_U = -80 \text{ W g}^{-1}$ for black carbon internally mixed with sulfate. In comparison, $G_L = -50 \text{ W g}^{-1}$ and $G_U = -90 \text{ W g}^{-1}$ for black carbon externally mixed with sulfate. (The calculations are for a specific scenario of surface albedo and particle number size distribution at 80% RH; see Figure 5, Lesins et al., 2002.) The percentage differences between G_U and G_L are 220% versus 80% for black carbon internally versus externally mixed with sulfate. This analysis suggests that $\Delta F_{U,L}$ reported by us for global aerosol direct radiative forcing is a lower limit; $\Delta F_{U,L}$ is expected to increase when black carbon internally mixes with sulfate.

13. Page 5423, line 14: there is a circa 30% difference in β_{avg} between the present paper and Koch et al. and Charlson et al. Is this really a "small" difference?

*** Original:

"Results of β_{avg} from our study and those from literature are given in Table 2. The 82 nm dry mode diameter on the US of the hysteresis loop most closely describes the common conditions employed in the literature. For this case, we obtain $\beta_{avg} = 11.7 \text{ m}^2 \text{ g}^{-1} \cdot \text{sulfate}$ with nitrate excluded. For comparison, β_{avg} is $11 \text{ m}^2 \text{ g}^{-1} \cdot \text{sulfate}$ in Chin et al. (2002), $8.4 \text{ m}^2 \text{ g}^{-1} \cdot \text{sulfate}$ in Koch et al. (1999), and $8.5 \text{ m}^2 \text{ g}^{-1} \cdot \text{sulfate}$ in the simplified treatment of Charlson et al. (1992). There is thus basic agreement among the models for β_{avg} . The small differences arise

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from differing treatments of aerosol optical and physical properties and also differences among global RH fields."

Revised:

"Results of β_{avg} from our study and those from literature are given in Table 2. The 82 nm dry mode diameter on the US of the hysteresis loop most closely describes the common conditions employed in the literature. For this case, we obtain $\beta_{\text{avg}} = 11.7 \text{ m}^2 \text{ g}^{-1} \cdot \text{sulfate}$ with nitrate excluded. For comparison, β_{avg} is $11 \text{ m}^2 \text{ g}^{-1} \cdot \text{sulfate}$ in Chin et al. (2002), $8.4 \text{ m}^2 \text{ g}^{-1} \cdot \text{sulfate}$ in Koch et al. (1999), and $8.5 \text{ m}^2 \text{ g}^{-1} \cdot \text{sulfate}$ in the simplified treatment of Charlson et al. (1992). The differences arise from differing treatments of aerosol optical and physical properties and also differences among global RH fields."

14. general technical comment: I find some of the figures really hard to read because they are very small: If there is a chance to put less figures on each page and enlarge them I would recommend doing this.

*** We agree that several of the figures and tables shown in APCD are small. We believe this results because APCD uses half-pages. In preparing the figures, we assumed full-page layout. Because APC uses full pages, the figures and tables should be of proper quality in APC. ***

Miscellaneous extra: 15. Response to an additional comment conveyed to us by Peter Adams during conversation at the AGU meeting in December 2003.

We have treated the particles as having constant refractive index, namely that of crystalline ammonium sulfate (1.46). However, the refractive index of water is 1.33 in the visible. Hence, while 1.46 accurately reflects dry particles on the LS of the hysteresis loop, aqueous particles on the US have a refractive index below 1.46. As RH increases,

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this value increasingly approaches 1.33 due to the higher water content (e.g., Figure 2 of Nemesure et al., 1995). Hegg et al. [1993] consider this problem in some detail.

We add the following paragraph to page 5434.

"The use of constant refractive indices independent of composition and hydration state (Table 2) systematically overstates scattering efficiency on the US of the hysteresis loop, implying that $\Delta F_{U,L}$ is an upper limit. As stated in Sect 6.3.2, optical depth and hence forcing is most strongly influenced by particles in the 50 to 70% RH range, for which the refractive index is estimated to be 1.43 and 1.40, respectively (cf. Fig. 2 for $\text{NH}_4\text{HSO}_4(\text{aq})$ in Nemesure et al. (1995)), as compared to 1.46 for the crystalline particles. Using the analysis of Hegg et al. (1993) (eq 2 therein), we conclude that scattering on the US of the hysteresis loop is reduced by 11% and 22% at 50% and 70% RH, respectively. The associated reduction on the LS of the hysteresis loop is smaller because the mass of the aqueous phase is smaller (cf. Figure 1c for the [0.8, 0.8] composition). The decrease in refractive index with increasing water content reduces scattering efficiency more on the US than on the LS. Therefore, the reported $\Delta F_{U,L}$, which does not account for this effect, is an upper limit."

Additional note: Given the length of the paragraphs added to the conclusions section, we changed the organization of the manuscript. Under the sensitivity analysis of section 6, we now collect many of the above paragraph into a subsection called "other factors," which is a more accurate description of these paragraphs. The remaining conclusions section is concise.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 5399, 2003.

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