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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.

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I thank Martin et al. for their response to my original comment and for the effort in making changes. However, the reply contains additional errors about the model of Jacobson (2001) and about its results. These issues are discussed below, and corrections are suggested.

1. ŞThe approach of Jacobson (2001) leads to 47 species which are entirely internally mixed.Ť

This statement is incorrect. The model treated 17 size bins, and each size bin had a different composition from each other, thus had its own mixing state relative to other size bins. It is only particles in a given size bin that were internally mixed (e.g., particles of the same size had the same composition). Particles of different sizes had different composition.

On the other hand, Martin et al.Šs criticism appears to apply to their own work. They appear to have treated chemistry of nitrate, sulfate, and ammonium in one size bin (and distributed the results among bins for optics only), thus they treated species chemically as entirely internally mixed in a bulk mixture, regardless of size. In reality, sulfate and nitrate almost always peak at different sizes. This factor and the fact that Martin et al. exclude most atmospheric electrolytes, renders their results about the solid composition of the atmosphere difficult to support.

2. ŞWe believe these predictions arise from a crossover in the internal mixing (e.g., NH4+ associated with SO42- is internally mixed with sea salt containing Cl-, so NH4Cl results. Similarly CaCO3 from dust combines with SO42- from industrial activitiesĚŤ

First, with regard to ammonium chloride, the mixing state assumed was clearly the most ideal. Over the ocean, where most ammonium chloride formed in the model, sea spray is internally mixed with most other particle types. For example, Murphy et al. (1998) found that almost all particles $>$0.13 mm over the remote Southern Pacific Ocean contained sea-spray. Andreae et al. (1986) found that 80-90 percent of silicate particles over the Pacific Ocean between Ecuador and Hawaii contained sea-spray. Most ammonium chloride that formed in the model was in the accumulation mode, where sufficient chloride exists over the ocean (Tables 2b, 3) and where most ammonium (even if associated with sulfate) resides over the ocean (Table 3). The results for ammonium chloride are certainly not settled, but Martin et al.Šs basis for disputing JacobsonŠs (2001) result for ammonium chloride based on mixing state appear misplaced.

Second, gypsum is almost certainly the leading sulfate solid in the atmosphere, and this can be demonstrated on the back of an envelope. There are three notable sources of calcium, not one. One is soil, where calcium is generally associated with carbonate but also with sulfate directly (e.g., gypsum is a soil that has worldwide deposits). The second is biomass burning, which emits both calcium and sulfate together. The third is sea spray, which is also a direct source of calcium and sulfate. Table 3 of Jacobson (2001) shows that, if one just looks at the mean observed Ca2+ and ssSO42- concentration over the southern ocean (which contains less Ca2+ than does the northern ocean because the northern ocean contains more soil dust sources), one sees that the gypsum formed from clean sea spray alone is about 0.9 mg m-3 (since gypsum forms once the RH drops below 98%). This is greater than the global average calculated value in Figure 2a (simply because one needs to weight the ocean area by the global area to get the global value). The relative concentrations of ammonium sulfate and ammonium bisulfate, which have much lower DRHs than gypsum (80% and 40%, respectively), were not close to those of gypsum, except in the upper troposphere and stratosphere, where all values were relatively small. Figure 3 of Martin et al. shows a globally-averaged sulfate concentration of 0.61-0.76 mg m-3. This would convert to a maximum of 0.78-0.98 mg m-3 of ammonium sulfate. Given the 80% DRH of ammonium sulfate, the fact that the ocean RH is not generally $<$ 80%, and the competition for sulfate by other components, it appears impossible, even with Martin et al.Šs numbers, for ammonium sulfate to be more concentrated globally than gypsum. As such, gypsum is almost certainly the most abundant yearly- and globally-averaged sulfate-containing solid worldwide.

3. ŞĚin general this extent of crossover is not so great in atmospheric particles.Ť The authors provide no evidence for this statement and it is contradicted by the references cited about mixing.

The proposed revisions in the text addressing the paper of Jacobson (2001) are fine, except the following changes are suggested.

1. In NEW PARAGRAPH, the statement ŞĚinto a combined description of 47 internally-mixed species,Ť would be more accurate if it read, ŞĚinto a combined description of

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47 species in each of 17 size bins of different composition.Ť

2. In NEW PARAGRAPH, the statements, ŞIn this paper, we dissectĚ However, similar informationĚŤ is misleading, since there are many differences between the two studies that are clear from the papers and clearly cause differences. Namely, the difference in the number of species (particularly solids), the treatment of multiple sizes versus a single size, RH treatment (instantaneous versus monthly average), and methods of calculating initial aerosol burdens for starters. It is suggested that the authors consider removing these last two sentences and consider listing the differences, such as those listed above, and state that these differences in methods may cause differences in results.

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