Atmos. Chem. Phys. Discuss., 8, S4309–S4312, 2008
www.atmos-chem-phys-discuss.net/8/S4309/2008/

Atmospheric Chemistry and Physics Discussions

ACPD

8, S4309–S4312, 2008

Interactive Comment

Interactive comment on "Do atmospheric aerosols form glasses?" *by* B. Zobrist et al.

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Received and published: 30 June 2008

This paper deals with the topical and exciting field of glassy or highly viscous aqueous solutions and provides convincing evidence that these particles may play a role in the Earth's atmosphere. While the formation of glassy materials is well studied in other fields, such as the food industry, our understanding of glass formation in the Earth's atmosphere is in its infancy.

In this paper Zobrist et al. use differential scanning calorimetry to map out the state diagrams of a number of atmospherically relevant aqueous systems. This significant body of experimental work will provide a very useful resource for future studies and I expect it to by highly cited.

This paper is of high quality and of an appropriate subject for ACP. I strongly recommend it is published as a full ACP paper, but only after the following concerns have been addressed.

Scientific concerns:

1) p 9265, ln16-19. These forcings are for liquid phase clouds only. The impact of ice nucleation is not included in the IPCC assessments. This should be made clear.

2) Fig 2. The solid black lines through the Tm data are the ice-liquid equilibrium curves. How was this data extrapolated to lower temperatures (the dashed line)?

3) Fig 2. These figures are very useful and will help the reader to understand the processes in the phase diagram. However, it should be noted in the text and the caption that these 'trajectories'; are idealised. For example, in panel c the concentration of the aqueous solution after ice nucleation and crystallisation would most likely not reach the equilibrium line as marked (point c). At temperatures well above the glass transition diffusion will remain very slow and crystal growth will be inhibited. In addition cubic ice may nucleate and crystallise and this will have a different ice-liquid equilibrium line. Trajectories through a similar state diagram were discussed in a recent article [Murray, Environmental Research Letters, v3, 2008].

4) p 9274 ln 8-15. In this discussion it is suggested that for a given wt% of solute, inorganics have a much larger impact on aw than organics. I think that this discussion makes more sense if it is based on mole fraction since aw is a colligative property. Only then can deviations from ideal behaviour be attributed to the nature of the molecules.

5) P 9275. ln 11. 'tendency to form glasses under T's and RH's relevant for the atmosphere'. I would replace RH's with compositions. There is an assumption made here that the droplets remain in equilibrium with the vapour phase. But in glassy droplets this is most likely not the case.

6) P 9279, ln 1-3. I do not agree that larger more hydrophobic molecules are more likely to form glasses. Large hydrophobic molecules will be insoluble and will therefore not promote glass formation. This caveat should be added.

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7) P 9280, ln 9-11. It is not clear from the text how this open blue triangle in plot 6b was obtained. I presume the authors took a dilute solution, saw ice nucleate and crystallise and then assumed that the droplets were at the ice-liquid equilibrium line as temperature was reduced and then saw a Tg. This is not an accurate way of determining Tg since the composition of the liquid portion of the droplet will become highly viscous on approach to Tg and the liquid will not remain in equilibrium with the ice and therefore the solute concentration will be lower than is assumed here. I suggest removing this data point.

8) P 9280, ln 28. 'agree nicely'; is not good scientific language. I suggest 'are consistent with the data'.

9) P 9282, ln 13-14. I suggest that 'but the data base is too small top draw any general conclusions' is deleted since a general conclusion is drawn concerning ring structures.

10) Figure 7. A value of Tg* for citric acid should now be added to Fig 7. Murray [ACPD, 2008] estimates that this is at 180 K, which is consistent with the other data on this plot. This supports the current results since Murray obtained freezing data with a different method to that employed here; this should be mentioned in the text.

11) P 9286 and Fig 9. In a number of places the authors refer to a glass transition occurring at a particular RH. They are making the assumption that the droplets are in equilibrium with the atmosphere in which case RH would be equal to aw. However, water will not be taken up into or lost from a glassy particle rapidly (as was discussed earlier in the manuscript) and therefore a glass transition will not take place at some prescribed RH and it does not make sense to discuss it in this way. If a glassy particle forms, it may not change composition with a change in humidity. Only increasing its temperature will allow it to take up water after passing over Tg. This is discussed by Murray [ACPD, 2008] in the atmospheric implications section (P8756-7). Figure 9 and associated text (and any reference to it in other places in the manuscript) needs to be substantially altered or deleted.

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12) Conclusion, part 2. I agree that typical atmospheric inorganic solutions do not form glasses as readily as organic solutions. However, I think it is wrong to claim that atmospheric aqueous inorganic droplets do not form glasses at all. Murray and Bertram recently published a study [Murray and Bertram, Phys. Chem. Chem. Phys., 2008, 10, 3287-3301(look at p3295)] of phases that form in ammonium bisulphate and letovicite compositions and here they suggested that the aqueous phase forms highly viscous or glassy material and this stabilises the metastable cubic phase. The ammonium bisulphate droplets do not form glasses under atmospheric temperatures, but letovicite composition solutions most likely do. This should be included in this discussion.

13) Conclusion, part 7. The reference to RH and glass formation should be removed.

14) P 9291, ln 17-20. I think this should be re-worded. This is not a proposal and while it is useful to think about implications we are a long way from understanding the role of glassy material sufficiently well to put it into global models.

Technical issues: 1) p9266, ln 22. 'aerosols'; should be aerosol.

2) section 2. This section needs to be broken down into more separate paragraphs. Paragraphs on the order of five sentences are much easier to follow. There are a few places in the paper where more paragraphs are required, I have not listed them all here.

3) p9277, ln 22. Avoid the use of the word 'quite' in 'quite accurate.'. In US English this means very accurate, whereas in UK English this means only reasonably accurate. The word quite causes a lot of confusion in science!

4) P 9295, ln 4-5. 'Once having these values' is not very good English, revision required.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9263, 2008.

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