

Interactive comment on “Measurements of the timescales for the mass transfer of water in glassy aerosol at low relative humidity and ambient temperature” by H.-J. Tong et al.

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Response to the comments by Anonymous Referee 2 on Atmos. Chem. Phys. Discuss., 11, 4843–4879, 2011

We thank the anonymous referee for taking their valuable time to review our manuscript and to make constructive comments. We have addressed the comments in our revised manuscript as specifically outlined below.

1. “One suggestion is that a little bit more relevance to the atmosphere and past studies be presented. . . .” The referee has requested a greater discussion of the relevance of these measurements to real atmospheric systems and we have attempted to achieve

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this in the new final paragraph of the Conclusions section of the manuscript, in particular establishing some guidelines for establishing the more general atmospheric importance of bulk diffusion limited particle size change. We have included the following discussion, which we copy here in its entirety:

“The measurements presented here and by Zobrist et al. (2011) have been made on coarse mode particles of radii greater than ~ 3 micrometres. An important issue to address is the relevance of these measurements to ambient atmospheric particles consisting of complex chemical mixtures and with a size in the accumulation mode. For example, while it has been inferred that ambient accumulation mode particles can exist in a glassy state (Virtanen et al., 2010), the timescale for water transport to and from such particles remains ill-defined. While the analysis presented here does not provide a comprehensive framework with which to assess the kinetic limitations imposed on ambient atmospheric aerosol particle size when existing in glassy or amorphous states, it is possible to establish some guidelines as to what must be considered.

(1) The kinetic limitation imposed on water transport between the gas and condensed phases is primarily associated with the diffusion constant in the particle bulk and is not simply related to the existence of a glass. This is shown both by the delayed time-response of particles even when above the glass transition RH and by the correlation of time-response with bulk viscosity for the mixed sucrose-sodium chloride aerosol. Although the kinetic limitations may be most severe at low temperatures, it is not simply an issue of bulk diffusion slowing mass transport at low temperatures. It is essential to assess the dependence of the viscosity/diffusion coefficients of water in aerosol as a function of composition, water activity and temperature.

(2) The time-response of aerosol particle size and composition to environmental change is dependent on the time history of RH and temperature. For example, slow changes in RH experienced by a particle will lead to a different response in the kinetically limited size than more rapid changes. This will require considerable further investigation.

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(3) While it is likely that accumulation mode particles rich in organic components will approach the equilibrium state on a timescale considerable shorter than coarse mode particles, the framework provided by Zobrist et al. (2011) shows that the relationship between the square root of time and particle size cannot be assumed, as would be derived from a simple Einstein relationship. Again, considerable further investigation is required.

(4) The time-response of particle size and composition observed here when the RH is increased to a value above the glass transition RH suggests that the process of humidification may lead to more rapid changes in particle size than would be expected from the low diffusion constants for water penetrating into the core of a glassy particle. The kinetics of size change are likely to be dependent on the rate of dissolution into a low viscosity aqueous shell that is at equilibrium composition with the surrounding water activity.

(5) It has been common to assume that the properties of aerosol measured in studies using flow tubes, HTDMAs, EDBs etc. (eg. hygroscopic growth) are governed by aerosol that exists in an equilibrium state. Although this is most likely the case for many measurements, determining the kinetic response of aerosol in any instrument is fraught with complications and the role of kinetic factors in limiting measured properties cannot often be entirely excluded.

While we do not consider that the measurements presented here and in Zobrist et al. (2011) represent a panacea for understanding the kinetic limitations imposed on water transport between the gas and condensed aerosol phases, they do indicate the importance of considering kinetic limitations further, particularly through controlled laboratory measurements.”

2. “I would also suggest that the authors give a little bit more thought to surface crystallization and very low mass accommodation coefficients as explanations for the observed behaviour.” We agree with the referee that it is likely that a very low mass ac-

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accommodation coefficient is unlikely to account for the observed behaviour. We do not believe, however, that surface crystallization is important. Even if crystallization were to occur, the requirement for ultraslow diffusion within the particle bulk is still essential to both prevent the particle as a whole from crystallising and for the mass transfer rate to remain slow.

We have included the following comment in the concluding section: “Kolb et al. (2010) have reviewed the current understanding of the uptake of gaseous phase molecules by an aerosol particle, separating out the limitations associated with surface accommodation (adsorption) and bulk accommodation (absorption), and highlighting the considerable uncertainty in even interpreting measurements of the condensation or evaporation of water (Miles et al., 2010). The measurements presented here are consistent with a slow diffusion rate for water in the bulk of the particle leading to the slow rate of mass transfer between the condensed and gas phases. This could be interpreted as implying a low value for the bulk accommodation coefficient, although reducing the problem to one value for this coefficient is probably over simplistic. It is also apparent that a low value for the surface accommodation/evaporation coefficient cannot be ruled out and could also lead to significant kinetic limitation being imposed on mass transfer. However, assigning the observed mass transfer impedance to an accommodation coefficient alone would mean a drastic change of this accommodation coefficient with solute concentration. While it is widely accepted that viscosity and diffusivity changes strongly with solute concentration, there is no indication for a similar effect in the accommodation coefficient.”

3. We have revised Figure 4, separating the inset in (a) into a separate panel so that the figure is easier to examine. We have also corrected the referencing to the figure and to spectra 3, 4 and 5. We hope that these changes make the figure easier to interpret. We have now ensured that we are consistent in using seconds throughout the text, although also include values in hours where it improves clarity. We are not sure what the reviewer refers to when they ask for the RH to be plotted on the x-axis.

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We have ensured that the discussion at the top of page 4856 is not contradictory, and are consistent in saying that the particle remains spherical. This is contrasted with what happens to a solution droplet when deposited on the coverslip.

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