

Interactive comment on “Chemical ageing and transformation of diffusivity in semi-solid multi-component organic aerosol particles” by C. Pfrang et al.

Anonymous Referee #2

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The authors report an application of their previously reported K2-SUB and KM-SUB models with some modest model development. A primary conclusion of the paper is that changes in particle diffusivity can be invoked to explain measured changes in condensed phase chemical loss rates. The paper describes the possibility of crust formation and the impacts of this on chemical transformations. The material appears suitable for publication in ACP, but there are a number of concerns that should be addressed prior to publication:

i) As the paper is written, it appears that the model considers only volatile and non-volatile components. Given oleic acid is unsaturated at C9, it might be expected that

C5461

C9 compounds will form as reaction products. Since there is no reference to the evaporation of reaction products, can the authors explain where any fragmentation products go? Ignoring semi-volatile components is clearly a very simplistic approach, and one that could substantially impact on the conclusions. If this is indeed the approach that is taken, a main concern is the dependence of the conclusions on the implicit assumptions in the model construction. The evaporation (and possible recondensation of components, though probably not under experimental conditions where gaseous components would only originate from particles) and resulting evolution of the chemical matrix over the timescales of the experiments need to be considered when interpreting such multiphase chemical processes. At least a thorough discussion of the reasons for making the assumption, its validity and implications of its use should be made.

ii) Representation of viscosity and diffusion in multicomponent mixtures is highly uncertain; in particular, the lack of miscibility across the full composition range as some components increase dramatically in viscosity may well lead to serious phase heterogeneity and separation into domains of very different compositions and viscosities. The obstruction theory approach taken in the current work is probably as good as is currently available. However, it would have been good to see a more substantial discussion of the sensitivity in the current application to the uncertainties inherent in this approach (e.g. there is no reason to expect only radial heterogeneity in viscosity; discrete domains analogous to micelle formation by surfactant material in aqueous solutions are equally as possible as complete crusts). It is acknowledged that the supplementary material uses an alternative approach based on an assumed difference in diffusion coefficient of products with respect to reactants. However, there is no discussion of the likelihood of either treatment within the bounds of possible multicomponent particle viscosity and diffusivity.

iii) There is little description in the methodology section concerning the initial conditions of the model. Indeed, the methodology section is much too brief and unclear. What are the 12 components in the mixed particle? Presumably they include all the reaction

C5462

products (lumped in some way) of oxidation of the particles as the evolution proceeds. What are the diffusivities of the individual components and how is the diffusivity of the mixture related to the individual components (i.e. what mixing rule is assumed?). Is it assumed that all components are homogeneously mixed throughout the particle (i.e. complete miscibility of all components)? On this note, would all components be expected to be homogeneously mixed throughout the bulk and surface layers and why? What is the RH of the simulations / experiments - how much water would be condensed at equilibrium? Was this equilibrium assumed to pertain at the start of the experiment? In the presence of components ranging in polarity, how would the surface energy contributions in the mixture lead to redistribution of components between the bulk and surface layers? If this study is part of a series of papers and the description of model setup is provided elsewhere in this series, there should be clear reference to where all this information is provided.

minor: comments such as "representative of atmospheric cooking aerosols" should be avoided, since the system under investigation is a very much simpler analogue of such particles. On the same subject, the work of Allan et al., 2010 definitely did not show that oleic acid was one of the most prominent reactive components of cooking aerosols (p13005). Similarity of AMS spectra cannot be used to infer molecular composition. The language in the current paper should not oversell the representativeness of the study. Individual unsaturated acids or mixtures of a few components are convenient model systems for study rather than representative of the majority of the mass of real atmospheric particles, whether well-established in the literature or otherwise.

technical: the dotted lines are only dotted at very high magnification and should be represented differently

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