



Gas uptake and chemical aging of amorphous semi-solid aerosol particles

Manabu Shiraiwa (1), Markus Ammann (2), and Ulrich Pöschl (1)

(1) Max Planck Institute for Chemistry, Biogeochemistry, Mainz, Germany (m.shiraiwa@mpic.de, +49-6131-305-487), (2) Paul Scherrer Institute, Villigen, CH-5232, Switzerland

Atmospheric aerosol particles may occur as solid or liquid or as a mixture of both depending on their compositions and ambient conditions. Carbonaceous combustion aerosol particles such as soot and related substances are known to be solid and undergo chemical reactions at the surface rather than in the bulk (black or elemental carbon, graphene, polycyclic aromatic hydrocarbons). Until recently, secondary organic aerosol (SOA) particles formed in the atmosphere from condensable oxidation products of volatile organic compounds were assumed to be liquid. Virtanen et al. (2010) [1], however, showed that biogenic SOA particles formed in plant chamber experiments and in new particle formation events over boreal forests can adopt an amorphous semi-solid state. Many organic substances, including carboxylic acids, carbohydrates and proteins, tend to form amorphous phases upon cooling or drying of aqueous solution droplets. Depending on viscosity and microstructure, the amorphous phases can be classified as glasses, rubbers, gels, or highly viscous liquids [2].

Here we demonstrate how molecular diffusion in the condensed phase affects the gas uptake and chemical transformation of semi-solid particles. Flow tube experiments show that the ozone uptake and oxidative aging of amorphous protein is kinetically limited by bulk diffusion. The reaction rate depends on the diffusion coefficients of both the gaseous and the condensed phase reactants, which can be described by a kinetic multi-layer flux model [3] but not by the traditional resistor model approach of multiphase chemistry. Based on numerical simulations, we present first spatial and temporal profiles of the concentration and reaction rate of ozone and reactive amino acid residues in an amorphous protein matrix. The chemical lifetime of reactive compounds in atmospheric particles can increase from seconds to days and more as the diffusion coefficients decrease over ten orders of magnitude from liquid to solid state. These results and related recent studies demonstrate that the occurrence and properties of amorphous semi-solid phases challenge traditional views and require advanced formalisms for the description of organic particle formation and transformation in atmospheric models of aerosol effects on air quality, public health, and climate.

Acknowledgements.

This work was funded by the Max Planck Society (MPG), Swiss National Foundation, and the European integrated project on cloud climate and air quality interactions (No 036833-2 EUCAARI). We thank M. Birrer, Y. Sosedova, and A. Rouviere for their help in the kinetic experiments; T. Koop and C. Pfrang for stimulating discussions.

REFERENCES

- [1] Virtanen, A., et al., An amorphous solid state of biogenic secondary organic aerosol particles. *Nature*, 467: p. 824-827, 2010.
- [2] Mikhailov, E., et al., Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations. *Atmos. Chem. Phys.*, 9(2): p. 9491-9522, 2009.
- [3] Shiraiwa, M., et al., Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone. *Atmos. Chem. Phys.*, 10(8): p. 3673-3691, 2010.