

Imaging and modelling trace metals in highly viscous organic aerosol particles

Peter A. Alpert¹, Jing Dou², Kevin Kilchhofer¹, Ulrich K. Krieger², Beiping Luo², Thomas Peter², Pablo Corral Arroyo³, Saša Bjelic⁴, Daniil Salionov⁴, Hartmut Herrmann⁵ and Markus Ammann¹

¹Laboratory of Environmental Chemistry, Paul Scherrer Institute, Villigen PSI, Switzerland

²Institute for Atmospheric and Climate Science, ETH Zürich, Zürich, Switzerland

³Laboratory of Physical Chemistry, ETH Zürich, Zürich, Switzerland

⁴Bioenergy and Catalysis Laboratory, Paul Scherrer Institute, Villigen PSI, Switzerland

⁵Atmospheric Chemistry Department (ACD), Leibniz Institute for Tropospheric Research, Leipzig, Germany

Heavy aerosol loading threatens human health across the globe and is typically related to photochemical processing associated with emission of organic, inorganic and trace metal compounds. Aerosol particles dominated by organic solutes may attain a high or ultra-high viscosity ($>10^{12}$ Pa s) becoming solid-like in cold and dry air, limiting diffusion of organic and reactive molecules through the particle volume, thus slowing chemistry. In contrast, illumination and thus photochemistry to produce radicals may occur through the bulk of light absorbing particles irrespective of diffusion limitations, but its efficiency is not well constrained. We investigated iron oxidation state changes in particles containing various concentrations of citric acid, iron(III) citrate, and copper(II) salts using environmental X-ray spectromicroscopy. Chemical images of aerosol particles with resolution currently as low as 35x35nm were acquired in a humidified microreactor revealing spatial gradients in the concentration of iron(II) and iron(III) compounds. We have also quantified the CO₂ formation from coated wall flowtube experiments due to decarboxylation subsequent to ligand to metal charge transfer and the condensed and gas phase products using proton-transfer reaction mass spectrometry to characterize the complex chemical reaction scheme. In the presence of copper, oxidation states of iron are expected to change. However, there is little information of reaction rates or equilibrium coefficients for copper-organic complexes. We will present ongoing work to better understand the interplay between copper and iron, and how this can affect redox cycling in organic aerosol. Such information is necessary for the accurate prediction of aerosol phase radical generation, chemical loss of oxygenated organic aerosol dominated by carboxyl functionalities and identifying diffusion limitations leading to the preservation of reactive oxygen species and free radicals.