

Imaging Single Aerosol Particles for Oxidation Chemistry and Reactive Species

PETER AARON ALPERT¹, PABLO CORRAL ARROYO^{1,2}, KEVIN KILCHHOFER^{1,3}, YANISHA MANOHARAN¹, JING DOU^{4,5}, ULRICH K KRIEGER⁴, SASA BJELIC¹, DANIIL SALIONOV^{1,6}, JOSEF DOMMEN¹, HARTMUT HERRMANN⁷ AND MARKUS AMMANN¹

¹Paul Scherrer Institut

²University of Bern

³ETH Zürich

⁴ETH Zürich

⁵University of Helsinki

⁶Ecole Polytechnique Fédérale de Lausanne

⁷Leibniz-Institut für Troposphärenforschung

Presenting Author: peter.alpert@psi.ch

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 viscosity ($>10^{12}$ Pa s) and solid-like in cold and dry air, limiting diffusion of organic and reactive molecules through the particle, thus slowing chemistry. In contrast, illumination and thus photochemistry to produce radicals should occur through the bulk particles irrespective of diffusion limitations. This is a unique aerosol chemical situation, where in-particle radical production depletes oxygen and faster than oxygen molecular flux and transport into the particle from the gas phase resulting in a (condensed phase) anoxic aerosol particle. However unintuitive, we argue this is the exact case for iron containing photoreactive particles. We measured iron oxidation state changes to track oxidation chemistry in single particles containing various concentrations of citric acid and iron(III) citrate using environmental X-ray spectromicroscopy and flow tube investigations. Chemical images of aerosol particles with resolution currently as low as $35 \times 35 \text{ nm}^2$ were acquired in a humidified microreactor revealing spatial gradients in the concentration of iron(II) and iron(III) compounds. We have also quantified the CO_2 production from coated wall flow tube experiments due to decarboxylation after ligand to metal charge transfer. The condensed and gas phase products are additionally characterized using proton-transfer reaction mass spectrometry to identify the complex chemical reaction scheme. We detected smaller molecular weight products that do and do not have carbon double bonds with both methods and are argued to form in anoxic and diffusion limited particles. In the presence of copper, results show that reactive species cause sharp gradients in iron oxidation inside particles and thus, oxidation overall. 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