Estimating amorphous deliquescence time scales of SOA from biogenic and anthropogenic precursors: Implications for heterogeneous ice nucleation on glassy aerosols.

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Recently, secondary organic aerosol (SOA) particles have been found to exhibit a highly viscous, amorphous state under atmospherically relevant conditions (Virtanen *et al*., 2010). Implications of such a glassy state are retardation of chemical reactions (Shiraiwa *et al*. 2011), incomplete gas-to-particle partitioning of semi-volatile constituents (Zelenyuk *et al*., 2012), and suppressed ice nucleation (Murray *et al*., 2008).

The actual phase state of SOA particles depends on several influencing factors such as composition, temperature and relative humidity. SOA comprises a multitude of complex mixtures of very different chemical substances. Typically, SOA is classified by precursor material (Hallquist *et al.*, 2009) and studies have shown that SOA from these classes exhibit differences in phase state under otherwise similar conditions (Saukko *et al*., 2012).

In atmospheric updrafts, which represent an important cloud formation mechanism, these particles may also deviate from humidification equilibrium, i.e. the agreement between ambient relative humidity and water activity inside the particle may not be established (Fig. 1). The degree of this temporal delay is governed by the rate of humidification, the particle size and the diffusivity of water inside the glassy organic particle matrix, which in turn depends on chemical composition, water content, and temperature.

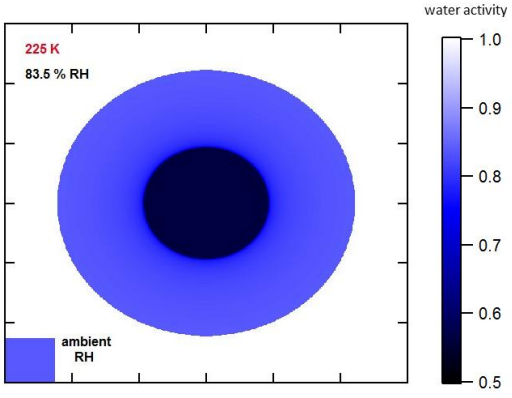

Figure 1. Partial deliquescence during an updraft simulation: While the surface is already liquid, the particle core remains glassy.

As recent studies have shown, glassy SOA particles may act as heterogeneous ice nuclei at low temperature (e.g. Murray *et al*., 2010). This new ice nucleation pathway might help explaining inconsistencies between measured and predicted relative humidities in the tropopause region.

Here we show how the delayed deliquescence of SOA particles can be quantified for several types of SOA and their surrogates by applying a kinetic flux model (Shiraiwa *et al*., 2012). Accompanying this model, we employ a novel methodology to estimate diffusivities from readily available glass transition and hygroscopic growth data. Using this approach we established a set of best guesses of these well-studied input parameters to investigate characteristic differences in low-temperature amorphous deliquescence between different SOA precursor classes and important surrogates, such as citric acid and sucrose.

Based on these parameterizations, we studied how the SOA particles' phase states and velocities of the respective deliquescence processes affect the particles' ice nucleation ability at low temperatures. These model simulations can be used to estimate upper temperature boundaries below which heterogeneous ice nucleation of glassy aerosols may occur as a function of humidification rates and particle size. A comparison between SOA from different precursors shows that this new ice nucleation pathway is more relevant for anthropogenic than for biogenic precursors.

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