Glass forming aerosol systems – precursors, processes and glassy products

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Amorphous liquid, semi-solid and glassy aerosol particles in the atmosphere are composed of many different substances and arise through various pathways (Hallquist et al., 2009; Jimenez et al., 2009; Marcolli et al., 2004). Here we focus on some exemplary systems for different pathways that lead to highly viscous aerosol particles, see Fig.1. We describe their glass-forming process as well as the first measurement of their corresponding glass transition temperatures T_g.

One way to semi-solid or glassy aerosol particles, at least under dry conditions, is the oxidation of volatile organic compounds (VOC) leading to secondary organic aerosols (SOA) (Hallquist et al., 2009; Jimenez et al., 2009). The particles' glass transition temperatures depend on their chemical nature and, hence, on the VOC precursors. Here we highlight two important SOA marker compounds, 3-methylbutane-1,2,3-tricarboxylic acid (3-MBTCA) and 2-methylbutane-1,2,3,4-tetrol, representing oxidation products of two major VOC species: α-pinene and isoprene. We synthesized both compounds and measured their respective glass transition temperatures. 3-MBTCA exhibits a T_g well above room temperature (Dette et al., 2014) and 2-methylbutane-1,2,3,4-tetrol shows a T_g of several ten degrees below 0 °C. These data agree well with recent in-situ studies over boreal forests showing that SOA particles composed of α-pinene oxidation products are in a semi-solid state (Virtanen et al., 2010) whereas SOA particles over tropical forests, which derive primarily from isoprene, exist more readily in a liquid state (Bateman et al., 2015).

Other VOC can form semi-solid or glassy aerosol particles via different pathways without being oxidized first. For example, glyoxal and methylglyoxal can be taken up by atmospheric water droplets and then form viscous aerosol particles upon drying by self-reactions in the aqueous phase which lead to the formation of oligomers (de Haan et al., 2009). Our measurements indicate that these particles have T_g values well within the atmospheric temperature range.

A third pathway to glassy aerosol particles are aqueous phase reactions between different compounds. Aldehydes such as glyoxal and methylglyoxal react with abundant inorganic species such as ammonium sulfate or ammonium bisulfate thereby forming mixtures of different oligomeric products (e.g. Galloway et al., 2014). These mixtures form amorphous particles under dry conditions with T_g values covering a wide temperature range from -50 °C up to room temperature and above, depending upon the aerosols' starting composition, the reaction conditions and the reaction time. Some of these mixtures form a one-phase mixture when dried directly after mixing but undergo liquid-liquid phase separation when dried some time after mixing. These two-phase mixtures accordingly show two glass transitions at different temperatures.

Finally, other non-reactive mixtures of organic and inorganic compounds can also form glasses under dry conditions just through the mixing process itself. We show that sodium nitrate and ammonium bisulfate form glasses with different organic compounds, with T_g values depending on the inorganic mass fraction (Dette and Koop, 2015). In some cases, e.g. in a mixture of 3-MBTCA and ammonium bisulfate, also liquid-liquid phase separation is observed resulting in two glassy phases upon cooling.

All these different processes lead to highly viscous or amorphous glassy aerosol particles, which may influence significantly the aerosol particles' chemical reactivity as well as their physical properties, thereby affecting their atmospheric behavior.

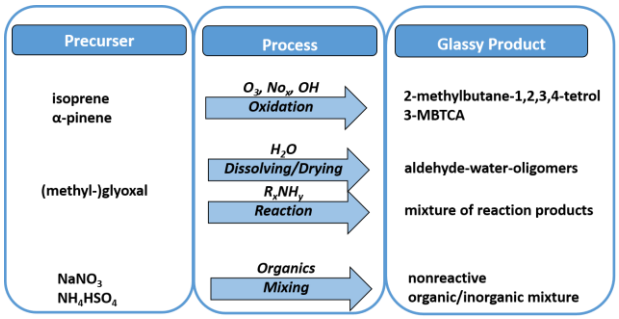

Figure 1: Glass forming systems, processes and products described in this work.

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