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Mixed-phased particles in polar stratospheric ice clouds

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The rate of chlorine activation reactions, which lead to ozone depletion in the winter/spring polar stratosphere (Molina, 1994), depends on the phase state of the surface of polar stratospheric cloud (PSC) ice crystals (McNeil et al., 2006). PSCs are thought to consist of solid ice and NAT (nitric acid trihydrate, $HNO_3 \cdot 3H_2O$) particles and supercooled $HNO_3/H_2SO_4/H_2O$ droplets. The corresponding PSCs are called Type II, Ia, and Ib PSCs, respectively (Zondlo et al., 1998). Type II PSCs are formed in the Antarctic region below the ice frost point of 189 K by homogeneous freezing of $HNO_3/H_2SO_4/H_2O$ droplets (Chang et al., 1999) with the excess of HNO3. The PSC ice crystals are thought to be solid. However, the fate of H^+, NO_3^-, SO_4^{2-} ions during freezing was not investigated.

Our differential scanning calorimetry (DSC) studies of freezing emulsified $HNO_3/H_2SO_4/H_2O$ droplets of sizes and compositions representative of the polar stratosphere demonstrate that during the freezing of the droplets, H^+, NO_3^-, SO_4^{2-} are expelled from the ice lattice. The expelled ions form a residual solution around the formed ice crystals. The residual solution does not freeze but transforms to glassy state at ∼150 K (Bogdan et al., 2010). By contrast to glass-formation in these nitric-acid rich ternary mixtures the residual solution freezes in the case of sulphuric-acid rich ternary mixtures (Bogdan and Molina, 2009).

For example, we can consider the phase separation into ice and a residual solution during the freezing of 23/3 wt% $HNO_3/H_2SO_4/H_2O$ droplets. On cooling, ice is formed at ∼189 K. This is inferred from the fact that the corresponding melting peak at ∼248 K exactly matches the melting point of ice in the phase diagram of $HNO_3/H_2SO_4/H_2O$ containing 3 wt % H_2SO_4. After the ice has formed, the glass transition occurs at Tg ≈ 150 K. The appearance of the glass transition indicates that the droplets do not freeze completely. After freezing, a fraction of each droplet remains liquid until its transformation to glass. The liquid, which remains unfrozen, is a residual solution formed by the expulsion of H^+, NO_3^-, SO_4^{2-} ions from the ice lattice during freezing. The residual solution undergoes the glass transition even if the cooling rate as small as 0.05 K/min (3 K/h) is applied. This cooling rate is similar to synoptic temperature change. Thus our results indicate that Type II PSC ice crystals cannot be completely solid, as is usually thought, but are enveloped by a supercooled $HNO_3/H_2SO_4/H_2O$ coating. These results also suggest that chlorine-activation reactions are better studied on supercooled $HNO_3/H_2SO_4/H_2O$ solutions than on a pure ice surface.

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