Multiphase Chemistry in the Cold

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Low temperatures and low relative humidity that may prevail over a large fraction of Earth in winter lead to aerosol with very low water content. Multiphase chemistry in such aerosol is significant, for example, in Asian winter haze events or Arctic Cities. However, our understanding of the rates and physical properties of these highly concentrated aerosol is incomplete. This work focuses on impurity deposits, such as sea salt aerosol, in snow. Snow's porosity guarantees the efficient gas exchange of reaction products with the overlaying air. Here, we investigate the freezing point and reaction rates of reactants embedded in this ideal natural reactor in the temperature range of 259 K to 240 K, most typical for the springtime Arctic, where chemistry in coastal snow is most active. Because these brine deposits share the high concentration with aerosol in the troposphere, results directly apply to wintertime haze.

The strategy of the experiments reported here was to probe the phase of sodium chloride–water samples at various positions in the phase diagram. Phase changes were observed in situ by Partial Auger-Meitner electron-yield NEXAFS spectroscopy (NEXAFS) at the Cl K-edge. We find sodium chloride at the interface of frozen solutions remains as supercooled liquid down to 240 K. Below this temperature, hydrohalite precipitates, for which we present the first NEXAFS spectrum. Taken together, this study reveals no differences in the phase changes of sodium chloride at the interface as compared to the bulk.

As temperature approaches the freezing point of such brines, thermodynamics dictates that concentrations of reactants in these aqueous patches increase ("freeze concentration effect"). Here we show how this does not always lead to increased reaction rates: We present results from a kinetic laboratory study on the oxidation of bromide in mimics of sea-salt aerosol embedded in snow. Our finding indicates that changes to the diffusivity of reactants and in the solubility of ozone in the aerosol counteracts the freeze concentration effect leading to an overall slower reaction rate.