The uptake mechanism of atmospheric hydrogen chloride gas in ice crystals via hydrochloric acid droplets

*Ken Nagashima[1], Gen Sazaki[1], Tetsuya Hama[1], Ken-ichiro Murata[1], Yoshinori Furukawa[1]

1. The Institute of Low Temperature Science, Hokkaido University

Ice has a great influence on the global environment, due to its abundance on the earth. Surfaces of ice have attracted considerable attention as "reaction sites" where atmospheric gases cause various chemical reactions in nature. Hence, so far there have been many spectroscopy studies on such chemical reactions on ice surfaces, yet revealing the uptake mechanism of atmospheric gases on/in ice remains an experimental challenge. Here we show that hydrogen chloride (HCl) gas, which triggers a series of chemical reactions that cause ozone depletion, is stored in ice crystals as droplets of an HCl aqueous solution.

We grew Ih ice single crystals on a cleaved AgI crystal from supersaturated water vapor in a nitrogen environment including 0.1% HCl gas (partial pressure of HCl gas P_{HCl} = 100 Pa). We directly observed ice crystal surfaces by advanced optical microscopy, which can visualize the individual 0.37-nm-thick elementary steps on ice crystals [1] (further details will be presented in "A-CC28: Glaciology" and "M-IS07: Growth and dissolution of crystal" sessions). Although the temperature of polar stratospheric clouds is -80 ˜ -70˚C, in this study we performed in-situ observation in the temperature range of -15 ˜ -1.5˚C, as the first step of systematic studies.

We found that the HCl gas induced the appearance of droplets of HCl solution on ice crystal surfaces [2]. Under supersaturated water vapor pressure, the HCl droplets were quickly embedded in the ice crystals during the growth of the ice. In contrast, under undersaturated conditions, the embedded HCl droplets reappeared on the ice crystal surfaces during the evaporation of the ice [3]. We estimated that the mole fraction of HCl incorporated into the ice as the HCl droplets (0.19% at -15˚C) was ten-times larger than the solubility of HCl gas in an ice crystal (0.017%). This picture of the uptake of HCl gas in ice is quite different from the conventional speculation in which HCl gas is confined to ice surfaces. Although the ranges of the temperature and the pressure of HCl gas in this study were higher than those in the polar stratospheric clouds, the insights obtained in this study may open a new avenue for the study of the uptake of atmospheric gases on natural ice.

[1] Sazaki et al. (2010) PNAS 107, 19702.
[2] Nagashima et al. (2016) Cryst. Growth Des. 16, 2225.
[3] Nagashima et al., submitted.

Keywords: Ice, Hydrogen chloride gas, Uptake mechanism, Advanced optical microscopy

