# Calcium speciation of particles trapped in Greenlandic ice core

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Ammonium sulfate ($(NH_4)_2SO_4$) is dominant species of sulfate aerosol (Pilinis et al., 1989), which causes indirect cooling effect by acting as cloud condensation nuclei (CCN) due to its high hygroscopicity. On the other hand, calcite ($CaCO_3$) in mineral aerosol reacts with sulfuric acid ($H_2SO_4$) and forms low hygroscopic sulfate, gypsum ($CaSO_4 \cdot 2H_2O$). It is possible that formation of gypsum in the atmosphere suppresses CCN activity of sulfate aerosol.

Greenlandic ice sheet preserves atmospheric particles and gases transported from continents in Northern hemisphere (Delmas, 1992). It is considered that determination of gypsum fraction to total calcium in mineral dust trapped in ice sheet formed in the various periods can indicate the degree of the reaction of calcite with $H_2SO_4$ in the atmosphere, which will allow us to know the CCN activity of sulfate aerosol in the past. In this study, calcium speciation of particles trapped in Greenlandic ice sheet was conducted.

Ice core sample was drilled at the southeast Greenland (SE Dome: 67.2°N, 36.4°W). Ice layers dated at 1971, 1978, 1987, 1995, and 2004 in the core sample were sublimated in low-temperature room (−20˚C) based on Iizuka et al. (2009). Calcium-bearing particles in the trapped particles were identified and their species were determined by micro X-ray fluorescence mapping and micro X-ray absorption fine structure spectroscopy, respectively.

Gypsum fraction to total calcium in 1971, 1978, and 1987 were lower than that of calcite. In contrast, the fraction of the two species showed opposite trends in 1995 and 2004. The results suggested that reaction of calcite with $H_2SO_4$ was more active in recent years. One of the major sources of mineral aerosol transported to Greenland is China (Bory et al., 2002). In China, amount of emission of sulfuric dioxide ($SO_2$: precursor of $H_2SO_4$) increased after 1970s, in contrast, that in North America and Europe decreased (Crippa et al., 2016). It is suggested that mineral particles transported to Greenland reacted with $H_2SO_4$ mainly emitted in China. In consequence, CCN activity of sulfate was suppressed in recent years especially in East Asia.