Calcium speciation of particles trapped in Greenlandic ice core associated with neutralization reaction of calcite in the atmosphere

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Aerosol has various influences on the surface environment of the earth, and one of the influences is its global cooling effect including direct and indirect effects. The indirect cooling effect is caused by hygroscopic aerosols which act as cloud condensation nuclei (CCN) and form clouds that can reflect sunlight. However, hygroscopicity of aerosol differs depending on the chemical species that constitute the particles. Therefore, it is important to clarify the chemical species in aerosols to estimate the degree of the indirect cooling effect. Sulfate, one of the major species of aerosols, has high CCN activity, because it is considered that most of sulfate is present as ammonium sulfate ($(NH_4)_2SO_4$) with high hygroscopicity (Pilinis et al, 1989). On the other hand, it is reported that calcite ($CaCO_3$) in mineral particles reacts with sulfuric acid (H_2SO_4) during atmospheric transportation and forms gypsum ($CaSO_4 \cdot 2H_2O$) (e.g. Jones and Prospero 1996; Takahashi et al., 2009). In our previous study, sulfate species of aerosol collected in Higashi-Hiroshima, Japan were determined, which suggests that atmospheric neutralization reaction of $CaCO_3$ in mineral dust with H_2SO_4 causes suppression of forming $(NH_4)_2SO_4$ decreases hygroscopicity of sulfate aerosols.

Greenlandic ice sheet preserved natural and anthropogenic trace gases and particles transported from continents in the Northern hemisphere (Delmas 1992), which is one of the important samples to reconstruct various factors on climate change of the past, and to contribute to the more accurate prediction of the climate in future. Therefore, determination of amount of $CaSO_4 \cdot 2H_2O$ in mineral dust, or identification of the neutralization process of $CaCO_3$, in ice sheet has a potential to reconstruct the variation of sulfate species in aerosols that have information of atmospheric chemical reactions in the past, which will help us to know the CCN activity of sulfate aerosols in the Northern hemisphere. However, there is no study on quantitative determination of $CaSO_4 \cdot 2H_2O$ in mineral dust in ice sheet. In this study, calcium speciation experiments of particles trapped in Greenlandic ice sheet were conducted.

Ice core were drilled at southeast Greenland, SE Dome (67.2˚N, 36.4˚W) in 2015. The parts of the ice dated as 1971, 1978, 1987, 1995, and 2004 were sublimated in low-temperature room (−20℃) to obtain trapped particles using the method in Iizuka et al. (2009, 2012). Calcium-bearing particles in the trapped particles were identified by micro X-ray Fluorescence (μ-XRF) mapping. Subsequently, calcium species of the particles were determined by micro X-ray absorption fine structure (μ-XAFS) spectroscopy.

As a result of the calcium speciation, $CaSO_4 \cdot 2H_2O$ fraction to total calcium in 1971, 1978, and 1987 were lower than $CaCO_3$ fraction. In contrast, $CaSO_4 \cdot 2H_2O$ fraction in 1995 and 2004 were higher than $CaCO_3$ fraction. It is considered that chemical reaction of $CaCO_3$ in mineral dust with H_2SO_4 was more active in recent 20 years. On the other hand, sulfate ion (SO_4^{2-}) concentration in ice core decreased from late 1970s. The trend of SO_4^{2-} was consistent with emission record of SO_2 in industrial countries at the time, however, emission amount of SO_2 increased in East Asia in recent 20 years, especially in China (Crippa et al., 2016), which is also an important source of mineral dust in Greenlandic ice sheet. Therefore, it was considered that calcium species in the mineral particles trapped in the ice sheet reflected chemical reactions of calcium with H_2SO_4 in China. These results suggested that suppression of $(NH_4)_2SO_4$ formation in the Northern hemisphere was associated with the neutralization reactions of $CaCO_3$ with H_2SO_4 in East Asia.

Keywords: aerosol, ice core, cloud condensation nuclei, neutralization reaction, calcium speciation, X-ray absorption fine structure (XAFS)

