

論文の内容の要旨

A study on clarification of reaction processes and sources of sulfate aerosol based on chemical speciation

(化学種解析に基づく硫酸エアロゾルの反応過程や起源の解明)

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Aerosols, one of important atmospheric components, are particulate matters suspended in the atmosphere giving significant impacts on various environmental issues. These issues include air quality related to their health effects and influences on ecosystem and their important roles in the Earth's climate. However, these impacts by various compounds in aerosols depend on the chemical species of each element in aerosols, which is a main viewpoint of this thesis. In **Chapter 1**, I provide introduction and aims of this study, which focuses on the effect of aerosols on the Earth's climate, types of aerosols related to chemical reactions examined in this study, and the method for the chemical speciation.

The effects of aerosols on the Earth's climate can be divided into direct and indirect effects. The latter, which is better written as indirect radiative forcing, is caused by aerosols acting as cloud condensation nuclei (CCN); aerosols alter cloud's properties such as reflection efficiency and lifetime, which enhances its negative radiative forcing (Albrecht, 1989; Lohmann and Feichter, 2010; Twomey, 1959). Such indirect radiative forcing by aerosols to cool the earth climate is considered to play a significant role to offset warming effects by greenhouse gases, but its estimation still has the largest uncertainty to predict the future climate (IPCC, 2013). CCN activity of aerosols depends largely on the species and their physicochemical properties of the particles such as particle size and hygroscopicity. Sulfate is a major component of aerosols which is mostly formed secondarily in the atmosphere through gas-to-particle conversion from anthropogenic sulfur dioxide (SO_2) as precursor

gases (e.g., Seinfeld and Pandis, 2006) Ammonium sulfate ((NH₄)₂SO₄) is considered as a dominate sulfate species in aerosols, because concentration of ammonia in aerosols is approximately equal to that of sulfate (e.g., Adams et al., 1999). (NH₄)₂SO₄ has high hygroscopicity with fine particle sizes. Consequently, sulfate aerosols can act as CCN and contribute largely to the indirect cooling effect (Bouche and Randall, 2013). However, the chemical forms of aerosols are variable by undergoing chemical reactions in the atmosphere referred to as “aging process.”

Mineral particles mainly emitted from natural sources account for about 30% of total aerosol mass globally (Sathesh and Moorthy, 2005), which can react with acids including SO₂ gases and sulfate in the atmosphere (e.g., Usher et al., 2003). Several mineral species in the particles are altered by aging process, which affects hygroscopicity of the particles. As a result, CCN activity of the mineral particles can either increase or decrease. Calcite (CaCO₃) is a highly reactive species in mineral particles with acids because of its high alkaline property (Al-Hosney and Grassian, 2005, 2004; Rubasinghege and Grassian, 2013; Usher et al., 2003). For example, reactions of CaCO₃ with nitric acid (HNO₃) or hydrochloric acid (HCl) form calcium nitrate (Ca(NO₃)₂) and calcium chloride (CaCl₂) in mineral particles, respectively, which increases CCN activity, because the reaction products have much higher hygroscopicity than that of CaCO₃ (Al-Hosney and Grassian, 2005; Goodman et al., 2000; Ma et al., 2012a; Sullivan et al., 2009; Usher et al., 2003). In contrast, CaCO₃ reacts with SO₂ and/or sulfate to form gypsum (CaSO₄·2H₂O) with similar hygroscopicity to original CaCO₃ and increase of the CCN activity is subtle (Gu et al., 2017; Ma et al., 2013; Tang et al., 2015; Usher et al., 2003). Instead, presence of CaSO₄·2H₂O in the particles formed by the reaction processes may overestimate the CCN activity of sulfate aerosol, since CaSO₄·2H₂O is less hygroscopic species (e.g., (NH₄)₂SO₄). Therefore, formation of CaSO₄·2H₂O can decrease of hygroscopic sulfate aerosols such as (NH₄)₂SO₄ due to decrease of SO₂ and/or sulfate concentrations in the atmosphere, and alters size distribution of sulfate aerosols because mineral particles and hygroscopic sulfate particles are generally distributed in large and fine size fractions, respectively. Thus, CaSO₄·2H₂O formation can affect various physicochemical properties of sulfate aerosols and hence their contribution to the earth climate. Therefore, it is necessary to identify sulfate species in aerosol and their size distribution with related processes in detail. However, there are few observation studies to observe the reduction of (NH₄)₂SO₄ by the formation of CaSO₄·2H₂O quantitatively in the field, though these processes are recognized in numerous studies in laboratory and in modelling (e.g., Dentener et al., 1996; Ma et al., 2013; Manktelow et al., 2010; Usher et al., 2003). In East Asia, emissions of anthropogenic materials including sulfate and mineral particles are significant relative to other regions (Crippa et al., 2016; Tegen and Schepanski, 2009). In addition, Asian dust contains much higher CaCO₃ than that of other regions (Krueger et al., 2004). Thus, it is important to investigate sulfate species in aerosols especially as well as their reaction and transportation processes in East Asia.

This thesis aimed to investigate the following three topics:

- (i) Speciation of sulfate in aerosols with various degrees of hygroscopicity and their concentrations in the atmosphere
- (ii) Effect of CaSO₄·2H₂O formation on the size distribution of sulfate aerosols and their CCN activity
- (iii) Emission sources, reactions in the atmosphere, and aging processes during transportation of sulfate aerosols

To achieve these goals, aerosol samples with finely-size fractionation collected at four sites in East Asia and ice core drilled at Greenland were analyzed using X-ray absorption near-edge structure (XANES) spectroscopy as a main analytical method which is a direct speciation method suitable to this study. This thesis consists of four studies (Chapters 2, 3, 4, and 5) with general discussion and conclusions (Chapter 6). Their contents were briefly given below:

Chapter 2. Sulfate species in aerosol collected in Higashi-Hiroshima

In this chapter, seasonal variation of sulfate species in aerosol was analyzed and their formation process was discussed. Total suspended particle (TSP) samples without size-fractionation were collected at Higashi-Hiroshima, Japan from September 2012 to August 2013. As a result of sulfur speciation by XANES, major sulfate species are those with high hygroscopicity except for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ fraction to total sulfate increased especially during a period of high concentration of Ca^{2+} of non-sea salt (nss) origin such as Asian mineral dust event in spring. Inversely, the amount of hygroscopic sulfate was decreased presumably by the reaction to form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by the reaction with CaCO_3 in the mineral dust. Subsequently, size-fractionated aerosol samples were collected at the same sampling site during winter (January 21 to 30, 2013), spring (March 4 to 9, 2013), summer (July 22 to August 5, 2013), and fall (November 11 to 25, 2013). As a result of Ca speciation analysis of the samples by XAFS, it was suggested that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was formed secondarily at the surface of the particles by the reaction of sulfate and/or SO_2 with CaCO_3 in the atmosphere.

Chapter 3. Analysis of Ca species of whole and at surface of individual aerosol particles between 2 sampling sites

To confirm whether $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was formed by the reaction of CaCO_3 , calcium (Ca) species of aerosols collected in Aksu (near source area of the mineral dust) and Qingdao (urban area in eastern China) during a large dust event recorded from 20 to 22 March 2002 were compared. Here, the depth-dependent Ca speciation using μ -XANES was for the first time applied to individual aerosol particles to investigate Ca species both in the whole particle and at surface of the particles to confirm the presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at the surface. The results directly showed that CaCO_3 was subject to reaction with sulfate in the atmosphere and formed $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at the surface of the particle.

Chapter 4. Analysis of particles transported and trapped in Greenland ice core sample related to secular change of SO_2 emission

Calcium species in particles trapped mainly in spring in an ice core at southeast Greenland were analyzed by Ca K-edge XANES using micro X-ray beam. The ice core has a record of aerosols from 1957 to 2014, and the samples corresponding to 1971, 1978, 1987, 1995, and 2004 were analyzed. As a result, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ fraction to total calcium in the ice core was larger in the recent layers (1995 and 2004) than those in the old layers (1971, 1978, and 1987), whereas CaCO_3 fraction indicated the opposite trend. The increase in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was consistent with the increase of SO_2 annual emission in China. Since it was reported by several geochemical studies using Sr, Nd, and Hf isotopes that mineral dust from China containing a larger amount of CaCO_3 compared with other areas is transported to Greenland in spring (Bory et al., 2003, 2002), the present data suggested that CaCO_3 included in Chinese mineral dusts reacted with sulfur components emitted in China and formed

CaSO₄·2H₂O, which was recorded in the ice core.

Chapter 5. Sulfate aerosols collected in Noto peninsula: estimation of their species, sources, reaction process, and roles for CCN

Size-fractionated aerosol samples were collected at the head of Noto peninsula from July in 2017 to May in 2018. This sampling site faces to the Sea of Japan, therefore it is good for observation of aerosols transported from Asian continent. In this chapter, seasonal variation of sulfate species and their transportation process with emission sources and aging process were investigated about the size-fractionated aerosol samples. Sulfur K-edge XANES spectroscopy for the samples revealed size and seasonal variation of sulfate species in the aerosols. As a result, it was suggested that CaSO₄·2H₂O formation in the coarse particles caused large reduction of hygroscopic sulfate in the finer particles. Besides, emission source of sulfate aerosol was discussed using [NO₃⁻]/[nss-SO₄²⁻] ratio, trace metal concentrations, and sulfur isotope compositions. Source of sulfate in coarse particles were mainly mineral particles and sea salts, and a part of them was considered to undergo reactions with anthropogenic sulfate components emitted from coal combustion in South China or domestic emission by oil combustion in Japan. On the other hand, sulfate sources of fine particles were considered to be biogenic emission and oil combustion in Japan during summer. In winter and spring, effects of oil combustion in Japan and coal combustion in south China were independently observed. Additionally, in the light of particle diameter and sulfate species, it was possible to discuss not only sulfate sources but also aging effects during transportation in the atmosphere by the combination of size distribution of sulfate, its source analysis, and speciation of sulfate in aerosols.

Chapter 6. General discussion and conclusion

In this thesis, the maximum reduction fraction of hygroscopic sulfate by the formation of CaSO₄·2H₂O was estimated as 33% of total sulfate during spring, which in turn suggested that the number concentration of cloud droplet number concentration (CDNC) decreased by 15.1% according to the relationship of mass concentration of sulfate to CDNC reported in Seinfeld and Pandis (2016). The reduction of CDNC can change the radiative forcing by +0.35 W/m² at maximum which is comparable to absolute value of the radiative forcing due to the indirect cooling effect of aerosols reported by IPCC (2013). It is suggested that the effect of the formation of CaSO₄·2H₂O on the indirect radiative forcing by sulfate aerosol should not be ignored. In addition, the reaction of the sulfate with CaCO₃ provided from East Asia is suggested to increase the low hygroscopic fraction in the global sulfate budget. The interaction of cloud-aerosol related to the indirect radiative forcing has still large uncertainties. For accurate estimation of indirect radiative forcing and prospect of future climate, the observational studies such as this thesis is important to determine and to justify parameters needed for more accurate estimation and prospect.