

Oral | Symbol A (Atmospheric, Ocean, and Environmental Sciences) | A-AS Atmospheric Sciences, Meteorology & Atmospheric Environment

## [A-AS22\_1PM2]Atmospheric Chemistry

Convener: \*Nobuyuki Takegawa(Research Center for Advanced Science and Technology, University of Tokyo), Yousuke Sawa(Geochemical Research Department, Meteorological Research Institute), Yugo Kanaya(Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology), Kenshi Takahashi(Research Institute for Sustainable Humanosphere, Kyoto University), Hiroshi Tanimoto(National Institute for Environmental Studies), Chair: Nobuyuki Takegawa(Research Center for Advanced Science and Technology, University of Tokyo)

Thu. May 1, 2014 4:15 PM - 6:00 PM 511 (5F)

This session provides a forum for the presentation of the broad spectrum of tropospheric and stratospheric chemistry, including various research topics (air quality and climate), approaches (modeling, field measurements, satellite data analysis, and laboratory studies), and species (gas and aerosol). This session also provides an opportunity for discussing possible future collaboration with other research fields relevant to atmospheric chemistry.

4:15 PM - 4:30 PM

## [AAS22-P02\_PG]Speciation of S and Ca species in aerosols with its relations to global cooling effects and processes of chemical reacti

3-min talk in an oral session

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Speciation of particles in aerosols is necessary to interpret what effects each species in the aerosols can have on environment. For example, global cooling effect by aerosols influences earth's climatic change (IPCC, 2007). In particular, sulfate aerosols are known to cool the earth by forming cloud condensation nuclei (CCN) because of their high hygroscopicity, which induces indirect cooling effect. Because the hygroscopicity differs depending on the species, sulfate speciation in aerosols is important for the determination of the magnitude of the indirect cooling effect. In this study, major ion concentrations in aerosol samples were measured by ion-chromatography. In addition, chemical species of calcium and sulfur in the each aerosol sample were determined using X-ray absorption near-edge structure (XANES) measured at BL-9A in Photon Factory, KEK. The speciation analyses can have some implications on the influence on the environment and the processes of chemical reaction of aerosols collected during several periods, such as (a) dust (Kosa) period (March 4-9, 2013), (b) the period with high PM2.5 concentration (Jan. 31-Feb. 1, 2013), and (c) the periods before and after (a) and (b). Major ion concentration data showed that  $\text{Ca}^{2+}$ , which is originated from soil, and  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , which were from human activities, increased in the period (a) compared with those in the periods before and after the period (a). On the other hand,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , which were emitted from human activities, increased in the period (b). In the period (a), it is considered that species originated from acids such as sulfate and nitrate which were incorporated into the particles increased in the samples whose aerodynamic diameter is over 1.0  $\mu\text{m}$ , because they have reacted with  $\text{CaCO}_3$  which was increased by Kosa event. In addition, from the fitting of XANES spectra, it was found that gypsum with low hygroscopicity were the main sulfur species in the

period (a), whereas  $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and hydrated sulfate with high hygroscopicity were main sulfur species in the period (b). Therefore, it is considered that when the concentration of  $\text{PM}_{2.5}$  increases, the indirect cooling effect can be large due to the large fraction of  $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and hydrated sulfate. On the other hand, the indirect cooling effect by sulfate aerosols can be smaller during the dust period due to the formation of non-hygroscopic gypsum by high amount of calcite in the atmosphere. Using the results of calcium and sulfur speciation both in the bulk and at the surface by fluorescence and conversion-electron yield detection, respectively, in the XANES analyses, we can discuss how chemical reactions occur at the surface of aerosol particles in each period. The abundance ratios of gypsum,  $\text{CaCO}_3$ , and  $\text{Ca}(\text{NO}_3)_2$  were different at the surface and the bulk. As a result, it was concluded that calcium species changes from gypsum,  $\text{Ca}(\text{NO}_3)_2$ , to  $\text{CaCO}_3$  from the surface to the core of the calcite particle. This results showed that (i) sulfuric acid from the atmosphere forms insoluble gypsum at the surface of calcite, (ii)  $\text{Ca}(\text{NO}_3)_2$ , formed as a result of the reaction of nitric acid and calcite, exists in the middle part, and (iii) unreacted  $\text{CaCO}_3$  remains in the core of the particle.