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Individual aerosol particles in and below clouds along a Mt. Fuji slope: Modification of sea-salt-containing particles by in-cloud processing

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ABSTRACT

Sizes and compositions of atmospheric aerosol particles can be altered by in-cloud processing by absorption/adsorption of gaseous and particulate materials and drying of aerosol particles that were formerly activated as cloud condensation nuclei. To elucidate differences of aerosol particles before and after in-cloud processing, aerosols were observed along a slope of Mt. Fuji, Japan (3776 m a.s.l.) during the summer in 2011 and 2012 using a portable laser particle counter (LPC) and an aerosol sampler. Aerosol samples for analyses of elemental compositions were obtained using a cascade impactor at top-of-cloud, in-cloud, and below-cloud altitudes. To investigate composition changes via in-cloud processing, individual particles (0.5–2 μm diameter) of samples from five cases (days) collected at different altitudes under similar backward air mass trajectory conditions were analyzed using a transmission electron microscope (TEM) equipped with an energy dispersive X-ray analyzer. For most cases (four cases), most particles at all altitudes mainly comprised sea salts: mainly Na with some S and/or Cl. Of those, in two cases, sea-salt-containing particles with Cl were found in below-cloud samples, although sea-salt-containing particles in top-of-cloud samples did not contain Cl. This result suggests that Cl in the sea salt was displaced by other cloud components. In the other two cases, sea-salt-containing particles on samples at all altitudes were without Cl. However, molar ratios of S to Na (S/Na) of the sea-salt-containing particles of top-of-cloud samples were higher than those of below-cloud samples, suggesting that sulfuric acid or sulfate was added to sea-salt-containing particles after complete displacement of Cl by absorption of SO_2 or coagulation with sulfate. The additional volume of sulfuric acid in clouds for the two cases was estimated using the observed S/Na values of sea-salt-containing particles. The estimation revealed that size changes by in-cloud processing from below-cloud to top-of-cloud altitudes were less than 6% for sizes of 0.5–2 μm diameter. The obtained results will be useful to evaluate the aging effect and transition of aerosol particles through in-cloud processing.

1. Introduction

Atmospheric aerosol particles play an important role in determining climate effects by their direct scattering and absorption of solar radiation while acting indirectly as cloud condensation nuclei (CCN) (e.g., Haywood and Boucher, 2000; Pilinis et al., 1995; Twomey, 1977). For estimation of their optical properties and characteristics of CCN, the size, concentration, and composition of aerosol particles are fundamental parameters, but they can be modified in the atmosphere by atmospheric aging and scavenging processes. Atmospheric aging processes of aerosol particles include adsorption and condensation of semi-volatile vapors, coagulation of particles with other pre-existing aerosol particles, heterogeneous reactions at the particle surface with gaseous species, and in-cloud processing in the atmosphere (Fuchs, 1964; Husar and Whitby, 1973;

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Mamane and Gottlieb, 1989; Meng and Seinfeld, 1994). In-cloud processing is absorption/adsorption of gaseous and particulate materials of activated particles as CCN.

The mass–size distribution of aerosols and their components (e.g., sulfate, elemental carbon and organic matter) is often observed as a bimodal distribution with mode peaks in less than 0.5 μm (condensation mode) and greater than 0.5 μm (droplet mode) (e.g., Huang and Yu, 2008; Meng and Seinfeld, 1994; Xiao et al., 2009). Generally, condensation, coagulation and heterogeneous reactions can modify the particle size to 300 nm at best. Consequently, droplet mode particle formation is regarded as a result of in-cloud processing. Meng and Seinfeld (1994), Kerminen and Wexler (1995), and Huang and Yu (2008) demonstrated numerically that in-cloud formation of sulfate is the only possible mechanism for growth of condensation mode particles to droplet mode particles. Although these studies were based on numerical analyses and ground-level observations of aerosol size distribution, some observations at sites near clouds have been conducted to investigate aerosol changes via in-cloud processing. The modification of the aerosol size distribution by in-cloud processing was traced empirically upwind, inside, and downwind from a hill-cap cloud in ground-based cloud passage experiments at Great Dun Fell, United Kingdom (Birmili et al., 1999; Bower et al., 1997; Choularton et al., 1997), on Tenerife, Spain (Bower et al., 2000), and at Mt. Thüringer Wald, Germany (Mertes et al., 2005). By comparing the upwind and downwind dry particle size distributions, differences in aerosol sizes were undetectable for particles with diameters greater than 300 nm. One reason might be that their relative diameter increase by the addition of soluble mass is smaller, and that the size distribution was affected by deposition along the forest canopy as dominating loss processes. Such reports underscore the difficulty of assessing the changes of size distribution of droplet particles in actual clouds.

In-cloud processing has been regarded as an effective process among aging processes of aerosol particles, but discussions of quantitative changes in actual clouds remain poor. However, several studies have assessed the compositional change of aerosol particles using individual particle analysis with electron microscopy (e.g., Nimura et al., 1998; Pósfai et al., 2003; Ueda et al., 2011a). Nimura et al. (1998) reported that some Asian dust particles obtained at Nagasaki were internally mixed with sea salt. They compared cloud conditions along the transport path based on satellite and trajectory, and reported that such dust particles containing sea salt were present abundantly in a case in which the air would have been influenced strongly by clouds in the maritime atmosphere during transport. Recent studies using microscopic analysis and based on field observations by aircraft or at high alpine sites have shown the composition of individual particles in clouds (Kojima et al., 2004; Kojima and Buseck, 2005; Li et al., 2011; Matsuki et al., 2010; Twohy and Anderson, 2008; Ueda et al., 2011b). Particularly, Matsuki et al. (2010) described differences of mixing states of sulfate, chloride, and nitrate on dust particles in and out of clouds, and suggested that the secondary species were particularly enhanced by in-cloud processing. As previous reports have described, some composition of individual particles can yield information about changes in particles caused by in-cloud processing. Using compositions of individual particles as the tracer, differences for particles before and after undergoing in-cloud processes might be assessed more quantitatively. However, details of comparisons of particles obtained before and after in-cloud processing have not been described in reports of those previous studies.

In this study, to elucidate the effects of processing in actual clouds, we conducted atmospheric observations along the slope of Mt. Fuji, Japan. Aerosol samples for microscopic analysis using electron dispersive X-ray were obtained in and below clouds, as particles before and after in-cloud processing. This paper presents discussion of effects of in-cloud processing based on differences of elemental compositions of individual particles on samples. Specific attention is devoted to processes that add sulfuric acid to particles during in-cloud processing.

2. Field observations and laboratory methods

2.1. Observation site

Observations at Mt. Fuji, Japan were conducted in July and August in 2011 and 2012, during the summer observation campaign period at the Mt. Fuji Weather Station (FWS), which is located at the summit (35.37°N, 138.73°E, 3776 m a.s.l.), and at Tarobo, which is located at the base of Mt. Fuji (35.33°N, 138.81°E, 1284 m a.s.l.). In previous studies, FWS was used to study the gases and aerosols in Mt. Fuji, Japan (Igarashi et al., 2004, 2006; Kaneyasu et al., 2007; Watanabe et al., 2008). In this study, the observations taken on foot were addressed along the mountain path from the summit to Tarobo using a portable optical particle counter and an aerosol sampler. According to cloud conditions of the day, the number concentrations and aerosol samples for analysis of elemental compositions were obtained at altitudes of the top of clouds (close above), in clouds, and immediately under clouds.

2.2. Number concentrations of aerosol particles and cloud droplets

The number–size distribution of atmospheric aerosol particles was measured using a portable laser particle counter (KR-12; RION Co. Ltd.). The laser particle counter (LPC) measures the number concentrations of aerosol particles for six size ranges: diameters greater than 0.3, 0.5, 0.7, 1, 2, and 5 μm. Aerosol particles were counted using the LPC after drying in a diffusion dryer at <30% RH. To quantify tendencies of cloud activation condition in clouds, aerosol number concentrations after removal of cloud droplets using an impactor (PIXI impactor) at the inlet were also measured as cloud interstitial particles. The 50% cut-off diameter (d_{50}) of the droplet-cut impactor stage was 5 μm at a flow rate about 2.73 $l \cdot min^{-1}$. The droplet-cut stage was changed manually every 2 min. In this study, the differences between the number concentrations with and without the droplet-cut stage were defined as the number concentrations of cloud droplets. The percentage of cloud droplets (number concentration of cloud droplet particles) to cloud droplets plus aerosol particles (number concentration without the droplet-cut stage) was estimated as the cloud droplet fraction.

2.3. Individual particle analyses using electron microscopy

Aerosol particles were collected for morphological analysis using a transmission electron microscope (TEM). TEM samples