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Mineral dust is a sink for chlorine in the marine boundary layer

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Abstract

Dust particles affect the budgets of important traces gases by providing a surface on which heterogeneous reactions can occur. The uptake of soluble species on dust alters the physical, chemical, and optical properties and the overall ability of dust to act as cloud condensation and ice nuclei. It is commonly assumed that all measured chloride in particulate filter samples is associated with sea-salt particles and any chloride in dust occurs as the result of internal mixtures of sea-salt and dust particles, formed by cloud processing. Here we show high temporal resolution data demonstrating the direct uptake of chlorine by dust via heterogeneous reaction with HCl(g). This reaction added significant amounts of chlorine to the dust particles during a major dust storm, representing 4–9% of the individual dust particle mass. Up to 65±4% of the dust particles contained chlorine due to this heterogeneous reaction during the dust front. Ignoring this process leads to an overestimation of sea-salt concentrations from bulk measurements, and an underestimation of the degree of sea-salt aging. The uptake of chloride will change the pH and hygroscopic properties of the dust and thus can influence the budgets of other reactive gases. Including this heterogeneous process in atmospheric measurements and chemical transport models will improve our ability to predict the atmosphere's composition and radiation budget with greater accuracy.

Keywords: Mineral dust; Heterogeneous chemistry; Chemical transport model; sea-salt aerosol; Single-particle analysis

1. Introduction

Mineral dust constitutes a substantial component of atmospheric aerosols, with total emissions ranging from 1000 to 5900 $\mathrm{Tg\,yr^{-1}}$ (Houghton et al., 2001). Mineral dust particles scatter and absorb solar and terrestrial radiation, and also alter cloud properties, and thus are important climate-forcing agents (Tegen et al., 1996; Sokolik et al., 2001; Satheesh and Moorthy, 2005). Radiative forcing by dust particles can range from −27.9 to 11.4 $\mathrm{W\,cm^{-2}}$

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(Sokolik and Toon, 1999), with uncertainties in these values due to complex chemical composition, shape, and evolution during transport.

Desert regions in China, especially those in the North, are sources of large amounts of atmospheric mineral dust particles. During the spring, massive dust storms develop over continental China (Sun et al., 2001), transporting dust particles from arid and semi-arid areas to several locations, including the North Pacific and sometimes even North America (Jaffe et al., 2003). In the spring of 2001 a large dust event occurred during the ACE-Asia campaign (Bates et al., 2004; Arimoto et al., 2006) and is the subject of the results presented here.

During long-range transport, the physical and chemical properties of mineral dust particles change due to heterogeneous reactions with trace gases, coagulation with other particles, and in-cloud processing (Andreae et al., 1986; Okada et al., 1990; Dentener et al., 1996; Niimura et al., 1998; Wurzler et al., 2000; Zhang et al., 2003). These processes affect the optical and hygroscopic properties of dust particles, and therefore influence their radiative (Sokolik and Toon, 1999; Sokolik et al., 2001; Satheesh and Moorthy, 2005), cloud nucleating (Levin et al., 1996; Rudich et al., 2002), and biogeochemical impacts (Houghton et al., 2001; Jickells et al., 2005). These processes also affect the cycles and chemical balances of important trace gases involved in the reactions (e.g. SO_2, NO_x, NO_y, O_3) (Dentener et al., 1996; Bauer et al., 2004), acid deposition, and the pH of precipitation.

Uptake and/or formation of nitrate and/or sulfate on mineral dust particles during transport has been observed in different locations (Fan et al., 1996; Jordan et al., 2003; Bates et al., 2004; Laskin et al., 2005; Matsuki et al., 2005), as well as in laboratory studies (Usher et al., 2003), and has been studied in several aerosol modeling efforts (Dentener et al., 1996; Bauer et al., 2004; Tang et al., 2004a, b). Associations of sulfate and nitrate with mineral dust particles, from sorption and/or oxidation, or cloud processing, affect the local cooling effect of the aerosols and modify the ability of the mineral particles to become cloud condensation nuclei (CCN) and ice nuclei (IN), also altering the lifetime of the dust particles (Levin et al., 1996; Rudich et al., 2002; DeMott et al., 2003; Fan et al., 2004). These associations shift the partitioning of soluble species from smaller sized particles into larger dust particles, thus reducing the hygroscopicity and CCN capability of particles in the accumulation mode ($D_a = 0.1$–$1.0\,\mu m$) (Tang et al., 2004a, b; Arimoto et al., 2006). Although the occurrence of sulfate and nitrate in dust particles has been previously observed, the presence of chloride in these particles has not been reported until recently (Zhang and Iwasaka, 2001; Arimoto et al., 2006; Murphy et al., 2006; Sullivan et al., 2007), since direct uptake could only be unambiguously confirmed using single particle analysis techniques.

The ACE-Asia intensive field operation (IFO) was conducted in March and April 2001 to investigate the wide-ranging atmospheric changes caused by Asian spring dust storms (Huebert et al., 2003; Arimoto et al., 2006). This campaign involved a variety of land, ship, aircraft, and satellite-based measurements as well as chemical transport modeling efforts. The results described here were obtained from online measurements of single-particles aboard the NOAA R/V Ronald Brown (RHB) during its research cruise through the Sea of Japan, during which it encountered a major dust storm originating in mainland China. Measurements of single-particle composition made by an aerosol time-of-flight mass spectrometer (ATOFMS) have provided new insights into the atmospheric processing of mineral dust. Arimoto et al. (2006) presented some preliminary ATOFMS results investigating the heterogeneous chemistry of mineral dust observed during the ACE-Asia campaign. These results were greatly expanded upon by Sullivan et al. (2007), including evidence for the uptake of chlorine-gases by dust. Asian mineral dust particles have the potential of neutralizing acidic species due to their intrinsic alkaline buffer capacity (Nishikawa et al., 2000; Usher et al., 2003; Tang et al., 2004b; Matsuki et al., 2005). Zhang and Iwasaka (2001) previously reported the presence of chloride in Asian mineral dust particles. They suggested it was not due to internal mixtures of sea-salt and dust but instead caused by heterogeneous reactions of chlorine gases with dust particles. Here we provide further evidence for this process with greater time and size-resolution and with supporting evidence from other measurements and modeling efforts made during the ACE-Asia IFO. This paper builds on the observations described by Sullivan et al. (2007) by examining the possible sources of the chlorine-gases in detail and provides strong evidence for HCl(g) released from aged sea-salt as the primary source of secondary chloride in dust. Results from simulations with the STEM-2K3 chemical transport model support the field observations. We