

Chlorine deposition on dust particles in marine atmosphere

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Abstract. A scanning electron microscope and an energy dispersive X-ray spectrometer were applied to analyze the particles collected during dust-storm events at southwestern Japan in spring 2000. Particle morphology and elemental composition were investigated and the weight ratios of different elements in individual particles were obtained. The results indicated that, besides the coagulation of sea-salt and dust particles, chlorine could deposit onto dust particles through the absorption of chlorine-containing gases when the particles passed through the marine atmosphere between China and Japan. The quantitative estimation revealed that the chlorine deposition on many particles was not negligible compared to sulfur deposition, suggesting that dust particles could remarkably modify the chlorine chemistry in marine atmosphere and possibly vice versa.

1. Introduction

Dust particles originating from arid and semi-arid areas are transported frequently out of continents, reach to remote marine areas and sometimes even arrive at other continents after crossing over oceans [Prospero *et al.*, 1981; Duce *et al.*, 1980; Uematsu *et al.*, 1983]. After leaving continents, air parcels containing dust particles mix with marine air, which leads to rapid variations of particle composition and morphology [Okada *et al.*, 1990; Fan *et al.*, 1996]. Since the geochemical mass cycle and radiative forcing associated with dust particles in the atmosphere are closely related to the physical and chemical properties of the particles [Uematsu *et al.*, 1983; Levin *et al.*, 1996], it is necessary to clarify what usually occurs on the particles during their long-range transport.

We collected particles during three dust-storm events at southwestern Japan in the spring of 2000 and the particles were analyzed individually. Compared to integrated sample analysis through which only average information of total collected particles were available, individual particle analyses could help us to obtain precise information about particles and learn what happened to them. Air parcels containing the collected dust particles passed over the Yellow Sea between China and Japan before they arrived at Japan. It has been widely known that nitrate and non-sea-salt sulfate can be efficiently formed on dust particles, and sodium and chlorine, through the mixing of

sea-salt and dust particles, frequently adhere to the particles when the particles appear in marine atmosphere [Okada *et al.*, 1990; Yamato and Tanaka, 1994]. These characteristics were confirmed in our analysis. More than these results, we found that chlorine (Cl) deposited onto dust particles not only through the coagulation of sea-salt and dust but also through the absorption of chlorine-containing gases. In this paper, we report this result and discuss the possible mechanisms of the deposition.

2. Particle collection and analysis

Particle collection was carried out on the roof of a 25-m high building at Kumamoto (134°45'E, 32°48'N) in southwestern Japan, on April 8, 12 and 27, 2000, when dust storms appeared. Particles were collected onto Pt electron microscope grids (3mm diameter) using a single-stage cascade impactor. The jet diameter was 1 mm, the flow rate of inlet air was 5 l min⁻¹, and collection time for each grid was 2 minutes. After particle collection, each grid was kept in a plastic capsule, which was then sealed in a plastic bag together with paper-packaged silica gel. Particles were investigated using the scanning electron microscope (SEM) of the Solar Terrestrial Environment Laboratory of Nagoya University for the observation of particle morphology. After a picture was taken, the elemental composition of each particle in the picture was determined by using the energy dispersive X-ray (EDX) spectrometer attached to the SEM. The EDX spectrometer is able to quantitatively detect the relative weight and atom ratios of elements (Z \geq 5 except nitrogen) in a single particle. The SEM was operated at 20 keV accelerating voltage and 120 μ A filament current. The X-ray spectrum of a particle was generated from a square covering the particle and was collected 50 live seconds with probe current of 0.3nA. After the spectrum of a particle was collected, the EDX equipments automatically specified the detected elements. The software Horiba Smedx was applied and the atom number fractions and weight fractions of different elements in individual particles were calculated by means of standardless method with ZAF correction. To avoid underestimating the content of sodium (Na), low energy correction was not preformed in the ratio calculation, resulting in unreasonably large ratios of carbon and oxygen and the ratio of Na was somewhat overestimated. In terms of elemental composition, dust particles mainly contain silicon (Si) together with/without other mineral elements, such as aluminum (Al), according to previous studies [Zhang *et al.*, 1993; Okada and Kai, 1995]. Sea-salt particles are abundant in Na and Cl and contain minor S and magnesium [Eriksson, 1959; Posfai *et al.*, 1996].

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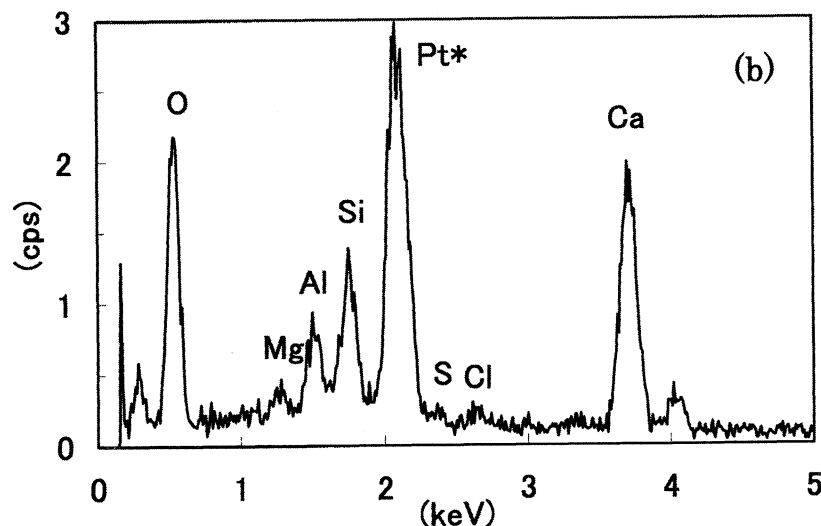
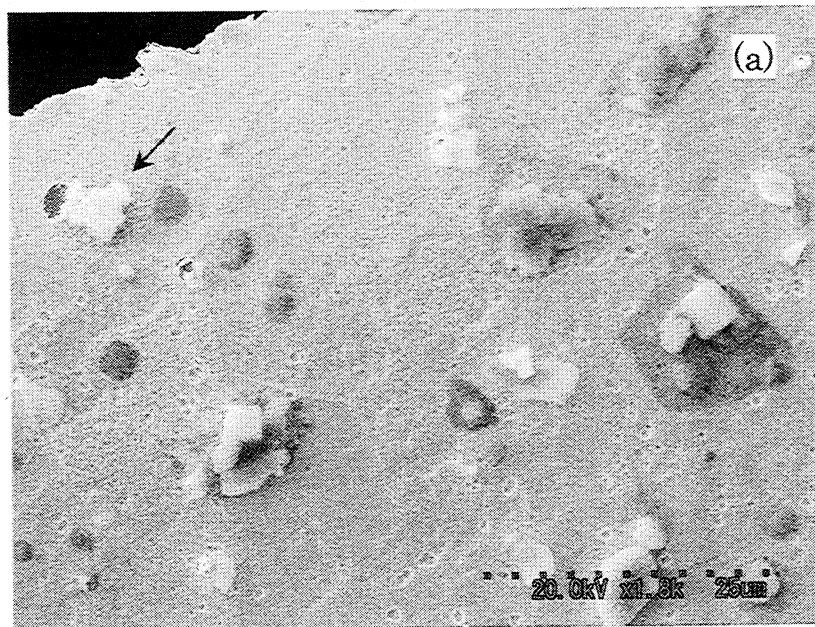


Figure 1. (a) A SEM picture of particles collected on April 12, 2000, and (b) the X-ray spectrum of the particle signed by an arrow in the picture. The picture shows the particles after dehydration, since both preservation with silica gel and analysis using electron microscopes could result in dehydration. The Pt peak in the spectrum was due to the sampling grid.

3. Results and Discussion

It was found that dust particles were predominant in the range of diameter $>1\mu\text{m}$. Figure 1 shows a representative SEM picture of collected particles and an example of X-ray spectra of dust particles. There were irregular shape particles and crystalline cubes. EDX analyses indicated that the crystalline cubes were sea-salt particles, some irregular particles contained mineral elements but did not contain Na (Na-free dust particles), and others contained both minerals and sea-salt suggesting they were the mixture of dust and sea-salt. Previous studies of individual particles revealed that dust particles were in irregular shapes, and sea-salt particles after dehydration were crystalline cubes [Iwasaka *et al.*, 1988; Parungo *et al.*, 1993; Posfai *et al.*, 1996]. Analyses of Asian dust particles collected over Japan and the northern Pacific indicated that dust particles were frequently mixed with sea-salt, sulfate and nitrate although few particles contained water-soluble components at and near their source areas in Asian continent [Okada *et al.*, 1990; Okada and Kai, 1995; Zhang and Iwasaka,

1999]. These features were consistent with our results. The most surprising result was that Cl was detected in many Na-free dust particles (Figure 1b). The absence of Na indicated that the particles were not disturbed by sea salt, suggesting the Cl deposition did not occur through the coagulation of sea salt and dust particles. Since Cl was not detected in dust particles and surface soils in the source areas of Asian dust [Kanamori *et al.*, 1991; Quan *et al.*, 1994; Zhang *et al.*, 1998], this result indicated that Cl deposited onto the dust particles through the absorption of Cl-containing gases. Non-sea-salt sulfate and nitrate formation on dust particles in the marine atmosphere was well known [Savoie and Prospero, 1989; Yamato and Tanaka, 1994]. In the extent of our knowledge, the formation of chloride on mineral particles has never been reported.

Table 1 lists the total number of analyzed particles and the detected dust particles in different cases, together with the numbers of the detected Na-free dust particles, of the detected Na-free dust particles on which the Cl-deposition was testified (Cl-deposited particles), of carbon-containing Na-free Cl-deposited dust particles, and of the mixture dust particles

Table 1. Number of the total analyzed particles and different kinds of dust particles.

Sampling date	April 8	April 12	April 27
Total analyzed particles	642	626	659
Dust particles	376	431	575
Na-free dust particles	62	149	63
Testified Cl-deposited dust particles among Na-free dust particles	38	60	35
Carbon-containing Cl-deposited dust particles among Na-free Cl- deposited dust particles	9	18	6
Na-containing dust particles of $\text{Cl/Na} > (\text{Cl/Na})_{\text{d-ssp}}^*$	182	80	132

* $(\text{Cl/Na})_{\text{d-ssp}}$ refers to the averaged weight ratios of Cl/Na in detected sea-salt particles in every case. It is 0.542 for April 8 (255 particles), 0.466 for April 12 (161 particles) and 0.531 for April 27 (67 particles).

whose weight ratios of Cl/Na were larger than the average Cl/Na of total detected sea-salt particles. Cl deposition occurred on about 50% of Na-free dust particles. It is worth noting that Cl/Na in many mixture particles were larger than that in detected sea-salt particles although the ratios (not shown here) in merely a few mixture particles were larger than that in seawater particles [1.625 from *McInnes et al.* (1994)]. Note the Na content in particles in the present study was overestimated. This result suggests either the chlorine deposition occurred or minerals depressed chlorine depletion from the sea-salt mixed in those particles.

In order to quantitatively evaluate the Cl-deposition, the relative weight ratios of Cl in Cl-deposited dust particles were depicted versus those of S in the same particles (Figure 2). It was found that the ratios of Cl/S in the particles were mainly from 0.2 to 2.0 and averaged at about 0.5, which means, if 2 units of mass of S had deposited onto a dust particle, about 1 unit of Cl might have simultaneously deposited onto the same particle. This also means that, if 2 atoms of S had deposited onto a dust particle, about 1 atom of Cl might have simultaneously deposited onto the same particle since the atomic weight of S is 32.1 and that of Cl is 35.5. Backward trajectory analyses indicated the collected particles were originated from the Asian continent, passed through the marine atmosphere between China and Japan, and arrived at southwestern Japan. It has been evident that dust particles rarely contained Cl and few contained S in the northwestern and northern areas of China [*Nishikawa et al.*, 1991; *Okada and Kai*, 1995; *Fan et al.*, 1996; *Zhang and Iwasaka*, 1999]. So the Cl and S deposition most possibly occurred after the particles met marine air. If this is true, the above results indicate that the Cl deposition was not negligible compared to that of S deposition in marine atmosphere.

There are three major gaseous species containing Cl in marine atmosphere: HCl, mainly emitted from sea-salt particles through Cl-replaced reactions [*Eriksson*, 1959; *McInnes et al.*, 1994] and part from anthropogenic sources [*Kaneyasu et al.*, 1999]; CH_3Cl , from ocean and tropical lands [*Graedel and Keene*, 1995; *Yokouchi et al.*, 2000]; and CFCs (chlorofluorocarbons), from anthropogenic sources [*Singh*, 1995]. From Table 1, it was learnt that most of the Cl-deposited particles were carbon-free. Besides, the EDX spectrometer did not detect fluorine in those particles. Thus, the Cl deposition could not be explained by the deposition of CFCs or CH_3Cl . The reasonable mechanism was the deposition dominated by HCl. It is certain that dust particles can absorb the strong acidic gas of HCl because they are highly alkaline. Since the air parcels containing dust particles had passed over many urban and industrial areas of the North China and South Korea before they arrived Japan, anthropogenic emission might have also contributed considerable HCl in the present cases. The fact that Cl was comparable to S in many Na-free particles suggests the

rate of the Cl deposition was comparable to that of S on those particles. Given that Cl deposited onto dust particles totally to form chloride and S to sulfate, our results indicate that, if 2 moles of SO_4^{2-} deposit onto dust particles, about 1 mole of Cl might deposit onto the same particles in marine atmosphere.

Previous analyses of integrated samples also showed significant enhancement of particulate Cl formation by dust particles. For example, from the case data of *Kanamori et al.* [1991], it could be learnt that, during some dust events at Nagoya in Japan, the weight concentration ratio of Cl^-/Na^+ in particulate matters was 5.3, which was much larger than the ratio in seawater particles (1.625), although the ratio in particulate matters at Nagoya was about 0.8 during non-dust periods. Similar features were also found in case studies at Nagasaki. But the features could not be testified in some other case data in the reference. This difference might be caused by the limitation of particle collection and analysis techniques applied in that study. If sea-salt occupied larger part of total aerosols compared to minerals, particulate Cl in integrated samples should be dominated by sea-salt Cl. As described previously, in mixture particles of our measurements weight ratios of Cl/Na were frequently larger than that of sea-salt particles in the same cases, indicating the possibility of Cl deposition on the mixture particles. If the amount of Cl deposited onto mineral particles was relatively much less than that in sea-salt particles, the deposition cannot be specified through the analysis of integrated samples.

4. Implication

The above results imply that the ignorance of Cl deposition on dust particles due to the absorption of gaseous Cl-containing species might lead to large uncertainties in studies associated with dust and the deposition needs to be evaluated. But so far, studies about the modification of dust particles in marine atmosphere mainly limited on their

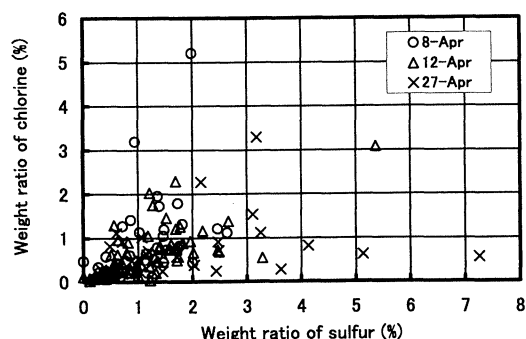


Figure 2. Relative weight ratios of Cl versus that of S in individual Cl-deposited dust particles.

interactions with sulfate, nitrate, sea-salt and clouds [Yamato and Tanaka, 1994; Dentener et al., 1996; Phadnis and Carmichael, 2000]. Chlorine deposition on dust particles, as well as sulfate formation, can make the particles more hygroscopic and subsequently stimulates their activities acting as condensation nuclei. At the same time, Cl chemistry in marine atmosphere must be modified. Dust particles would provide a sink for HCl when the particles appeared in marine atmosphere and the transfer of Cl from sea salt to dust particles would occur. The transfer cannot be evident in the data obtained from integrated samples, and this would lead to an underestimate of the amount of Cl lost from the sea salt. While that Cl would presumably not be re-released to participate in any gas-phase reaction, the fact that it was lost from the sea-salt particles would be significant. In addition, chloride formation will change the optical properties of dust particles since dust particles mixed with different species have dramatically different optical properties [Levin, 1996]. It must be noted that mineral dust has worldwide sources and contributes nearly half of global total atmospheric aerosols [Duce et al., 1991]. Through long-range transport, mineral dust is being constantly input from Africa to the Atlantic and from Australia to the Indian Ocean besides from Asia to the Pacific. Comprehensive studies have suggested that the radiative forcing due to dust activities possibly have very important climatic effects [Tegen et al., 1996; Sokolik and Toon, 1996]. Therefore, incorporating Cl chemistry in field measurement and numerical simulation associated with mineral dust might be inevitable for improving our understanding of dust's impacts on regional and global atmosphere.

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