Hygroscopic mineral dust particles as influenced by chlorine chemistry in the marine atmosphere

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2   chemistry in the marine atmosphere

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1 **Abstract**

2

3   Morphology and elemental compositions of individual dust particles were

4 investigated with the use of Asian dust samples collected at a site along the Sea

5 of Japan side of the archipelago. Our results indicate the preferential formation

6 of chloride in Ca-containing dust particles (0.1 < Cl/Ca < 0.65) in cases when

7 the particles contain little or no sulfate. Such particles account for more than

8 two-thirds of the sea salt-free dust particles found in the samples. Most of them

9 are in an amorphous state and nearly spherical even under high vacuum. A likely

10 explanation for the results is that highly soluble salts such as calcium chloride

11 ($CaCl_2$) are formed as a result of heterogeneous reactions of dust particles with

12 chloride precursor gases (mostly, HCl) in the marine atmosphere. The chloride

13 formation is expected to play an important role in enhancing the hygroscopicity

14 of dust particles.

1. Introduction

Morphology and compositional changes of mineral dust particles in the process of being transported in the atmosphere have an important impact on both the Earth's albedo and climate. For example, heterogeneous chemistry of dust particles with acidic gases such as NO_y (e.g., HNO_3, N_2O_5) and SO_2 will alter the hygroscopic properties of the particles. So far, a number of both laboratory and field studies have focused on the conversion of insoluble calcium carbonate ($CaCO_3$) to highly soluble salts such as calcium nitrate ($Ca(NO_3)_2$) via heterogeneous chemistry on dust surfaces [*Krueger et al.*, 2004; *Laskin et al.*, 2005; *Matsuki et al.*, 2005; *Hwang and Ro*, 2006]. Although many types of dust particles are considered to modify the radiative properties of clouds by acting as efficient heterogeneous ice nuclei (IN) [*DeMott et al.*, 2003; *Möhler et al.*, 2006], dust particles coated with soluble materials have the potential to act as cloud condensation nuclei (CCN) at commonly found supersaturations [*Levin et al.*, 1996; *Kelly et al.*, 2007].

Several field measurements have reported the formation of chloride in dust particles, which they attribute not only to internal mixing processes of dust particles with sea salt particles [*Zhang et al.*, 2003] but also to heterogeneous chemistry of dust particles with chloride precursor gases [*Zhang and Iwasaka*, 2001; *Murphy et al.*, 2006; *Sullivan et al.*, 2007]. *Kelly and Wexler* [2005] have proposed that $CaCO_3$ in dust particles could react with HCl in the atmosphere via the following heterogeneous reaction pathway:

$$CaCO_3 \text{ (s)} + 2HCl \text{ (g)} \rightarrow CaCl_2 \text{ (aq)} + H_2O \text{ (aq)} + CO_2 \text{ (g)} \qquad (1)$$
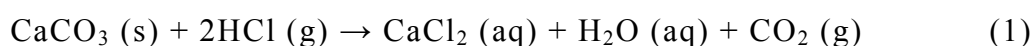
Nevertheless, there is an incomplete understanding of heterogeneous chloride formation involving dust particles in the atmosphere, and there are very

1   little data about its subsequent effects on the particle properties. In this study,

2   we present direct observations of individual dust particles at a local site along

3   the Sea of Japan. The present results provide field evidence indicating that the

4   heterogeneous production of highly soluble chloride in dust particles could be a

5   significant process for the change of dust hygroscopicity and morphology as

6   well as chemical composition.

7

8   **2. Data and Methods**

9

10   Aerosol sampling was conducted on the roof of a 33-meter high building of

11   Kanazawa University (36°32'N, 136°42'E, 115 m above sea level), located on a

12   rural hill site along the Sea of Japan (see Figure 1a). Aerosol particles were

13   collected by introducing sample air into a two-stage cascade impactor at a flow

14   rate of 1.2 L min^{-1}. The first and second stages of the impactor have nozzle

15   diameters of 1.3 and 0.4 mm, respectively. The aerosol samples used here were

16   obtained from the first stage on which carbon-coated nitrocellulose (collodion)

17   films supported by Ni mesh grids were installed. The 50% cut-off diameter of

18   the first stage is 1.1 µm assuming particle densities of 2.2 g cm^{-3}. Number

19   concentrations of particles with equivalent optical diameters (D_p) > 0.3, 0.5, 0.7,

20   1.0, 2.0, and 5.0 µm were measured by using a handy optical particle counter

21   (RION, KR12A).

22   The particles were analyzed manually using conventional scanning electron

23   microscopy with energy dispersed analysis of X-rays (SEM/EDX). The basic

24   operation of the SEM/EDX for single particle analysis has been described

25   previously [*Zhang and Iwasaka*, 2001; *Zhang et al.*, 2003] and is only briefly

26   summarized here. After examining the size and morphology of single particles

27   microscopically, the X-ray spectrum from each particle was acquired for 40 sec

28   of live time, at a beam current of 0.2 nA and an accelerating voltage of 20 kV.

The relative composition (normalized atomic percent) of elements with atomic number (Z) $\geq$ 11 in each particle was calculated using ZAF (Z: Z-dependent electron scattering, A: absorption, F: fluorescence) matrix correction. Since low energy correction was not applied in the calculation, the relative composition of Na tends to be somewhat overestimated [*Zhang and Iwasaka*, 2001; *Zhang et al.*, 2003]. In this study, the relative composition of low-Z elements such as C, N, and O was not determined.

The particles were classified based on the relative composition of elements as dust and sea salt particles. Dust particles typically consist of crustal elements such as Si, Al, Fe, Ca, Mg, and Na. Although most dust particles tend to contain only small amounts of Na and Mg, those internally mixed with sea salt contain large amounts of Na and Mg [*Zhang et al.*, 2003]. Sea salt particles consist mainly of Na and Mg, together with Cl and S. Here we focus on the uptake of chloride precursor gases by dust particles during atmospheric processing. In order to select sea salt free-dust particles, only particles meeting the criterion of "Al + Si + Fe > 0", "Na $\approx$ 0 (the K-line peak does not exceed the background signal in the X-ray spectrum)" and "Mg < Si" were classified as dust particles. Also, Na-dominant particles meeting the criterion of "(Na + Cl)/(Na + Cl + Al + Si + Fe) > 0.65" were classified as sea salt particles.

3. Results

Mineral dust samples were collected at 06:00-06:05 UTC (= LST – 9 hours) on 21, 23, and 24 April 2007. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://www.arl.noaa.gov/HYSPLIT.php) is used to estimate the backward trajectories for the observation period (Figure 1a). There are no substantial sources of dust particles in the vicinity of the sampling site, making it likely that most of the particles were transported from its upwind

areas such as desert and/or loess areas in the Asian continent. The number concentrations of fine ($0.3 < D_p < 1.0$ μm) and coarse ($D_p > 1.0$ μm) particles are illustrated in Figure 1b. The collected particles consisting of dust and sea salt components were present in the coarse mode, and the concentrations of coarse particles slightly increased during the 21-24 April sampling period. On the other hand, the concentrations of fine particles did not increase simultaneously. Note that a majority of fine particles found around this area are usually secondary particles consisting largely of sulfate [*Bates et al.*, 2004]. Thus, it is expected that the sampling site was under relatively unpolluted conditions by sulfur compounds during this period.

The relative elemental ratios of single dust particles found in the samples are plotted in Ca:Cl:(Al + Si + Fe) and Ca:S:(Al + Si + Fe) ternary diagrams in Figure 2. These results are summarized in Table 1. The presence of chloride was found almost exclusively in Ca-containing dust particles collected on 21 and 24 April 2007 (see Figure 2a). Such dust particles accounted for about 68% of the sea salt-free dust particles in the samples, and a majority of them lay inside of the region for $0.1 < Cl/Ca < 0.65$. About 74% of the dust particles containing chloride accompanied small amounts of sulfate, but about 26% of them were free of sulfate. In contrast, the existence of both chloride and sulfate was rarely detected in dust particles collected on 23 April 2007 (see Figure 2b). We also analyzed dust particles collected on 9 April 2007 (not shown here) and found that most of the particles contained large amounts of sulfate but almost no chloride.

The micrographs of a typical dust particle containing chloride were obtained at different electron voltages in the high-vacuum SEM chamber (up to ~10^{-3} Pa). This approach is applied to the determination of the morphology and phase changes of $CaCO_3$/$Ca(NO_3)_2$ particles [*Laskin et al.*, 2005]. As illustrated in Figure 3, at higher electron voltage (20 kV), an insoluble component of the

1   particle (e.g., aluminosilicate, carbonate) is electronically opaque (bright). In

2   contrast, its surrounding part appears nearly transparent (dark), and it is

3   probably made up of soluble components. The morphology of the entire particle

4   appears to be spherical at lower electron voltage (1.5 kV). It is therefore likely

5   that the dust particle was present as a droplet, or at least coated with aqueous

6   solutions, in the atmosphere. We found that almost all of Ca-rich dust particles

7   coated with chloride in the samples collected on 21 and 24 April 2007 were in an

8   amorphous state and nearly spherical, while dust particles of crustal origin are

9   generally in an irregular shape.

10

11   **4. Discussion**

12

13   It is noteworthy that the formation of chloride was confirmed preferentially

14   in Ca-containing dust particles in the samples collected on 21 and 24 April 2007.

15   As previously mentioned, these particles are sea salt-free dust particles; hence,

16   internal mixing processes of dust with sea salt particles should be excluded as a

17   cause of the chloride formation. Also, what is important is that most of the dust

18   particles were coated with highly soluble materials. A likely explanation for the

19   present results is that Ca-containing compounds such as carbonate making up

20   dust particles are favorable for the uptake of chloride precursor gases (mostly,

21   HCl) and that the products of this reaction are hygroscopic salts.

22   The release of HCl into the atmosphere is primarily due to the acidification

23   of sea salt particles [*Graedel and Keene*, 1995]. The relative elemental ratios of

24   sea salt particles collected on 21, 23, and 24 April 2007 are plotted in Na:S:Cl

25   ternary diagrams in Figure 2. Fresh sea salt particles containing large amounts

26   of chloride were predominantly found in the samples of 23 April 2007 (see

27   Figure 2b). We note the fact that there was the passage of a rain front over the

28   sampling site from 05:00 to 16:00 UTC on 22 April 2007. It is assumed that

trace acidic gases (e.g., NO_y, SO_2, HCl) could be removed from the atmosphere

by precipitation (up to 4.0 mm hour^{-1}) during the passage of the rain front, so

both dust and sea salt particles in the postfrontal air masses (i.e., just after the

passage of the rain front) could maintain their original composition without

chemical reactions during long-range transport. In contrast, sea salt particles

collected on 21 and 24 April 2007 became depleted of a greater or lesser degree

of chloride (see Figure 2a), indicating the release of HCl from the particles.

Since the chloride-depleted sea salt particles were found together with dust

particles coated with chloride, the release of HCl from sea salt might play a role

in the formation of chloride in dust particles.

Sullivan et al. [2007] have reported that the chlorine uptake by dust particles

can be attributed to the release of unusually large amounts of HCl from sea salt

particles, which are acidified by H_2SO_4 formed from the oxidation of volcanic

SO_2. However, it is doubtful whether sea salt particles as presented in Figure 2a

had the potential to produce large amounts of HCl. This is because the aerosol

samplings were conducted under relatively unpolluted conditions by sulfur

compounds, and the degree of chloride depletion in the sea salt particles was not

so significant.

Under heavily polluted conditions by sulfur compounds, Cl will be driven

out of sea salt particles leading to enhanced HCl concentrations, but carbonate

components will also be driven out of dust particles and be replaced with

sulfate; hence, the formation of chloride in such dust particles should be hard to

take place. For instance, dust particles found in the samples of 9 April 2007

rarely contained chloride. Under relatively unpolluted conditions by sulfur

compounds, however, the replacement of carbonate with sulfate will be

suppressed. We consider that the observations on 21 and 24 April 2007 were

made under such conditions. So what is important for the formation of chloride

in dust particles is presumably an intermediate level of sulfate (or nitrate) that is

1 enough to liberate Cl from sea salt particles and that cannot liberate all

2 carbonates from dust particles.

3   The preferential formation of highly soluble chloride in Ca-containing dust

4 particles has important implications for their hygroscopic properties. Here we

5 examine whether $CaCO_3$ has the potential to be transformed into aqueous $CaCl_2$

6 solutions via heterogeneous reaction $CaCO_3 + 2HCl$ under given conditions of

7 the atmosphere. Figure 4 shows the equilibrium concentrations of HCl as a

8 function of water activity for the reaction $CaCO_3 + 2HCl$. (Under equilibrium

9 conditions water activity in aerosol particles is equal to the ambient relative

10 humidity (RH)). The calculations of the equilibrium concentrations follow *Kelly*

11 *and Wexler* [2005]. Here we choose temperatures of 0-30°C and pressures of

12 1000-700 hPa (approximately equivalent to 0-3 km altitudes). The equilibrium

13 concentrations of HCl for the reaction $CaCO_3 + 2HCl$ decrease exponentially

14 with increasing water activity (i.e., RH) and with decreasing temperature, while

15 they do not make much difference at pressure altitudes between 1000 and 700

16 hPa.

17   The reaction behavior of the chlorine uptake by dust particles depends on the

18 previously experienced chloride precursor gases, RH, temperature. For example,

19 measurements of HCl on Oki Island in the Sea of Japan showed the highest

20 concentrations of 515±214 pptv HCl in the westerly continental flow and the

21 lowest concentrations of 107±23 pptv HCl in the northerly flow [*Kajii et al.*,

22 1997]. Even in remote oceanic areas, concentrations of 100-300 pptv HCl have

23 commonly been observed [*Graedel and Keene*, 1995]. The RH measured at

24 Kanazawa during 21-24 April 2007 typically varied between about 40 and 90%

25 at a temperature of 10 to 20°C. Assuming that there are mean concentrations of

26 >100 pptv HCl in the marine atmosphere, the mean concentrations of HCl are

27 greater than the equilibrium concentrations of HCl for the reaction $CaCO_3 + HCl$

28 under these conditions, suggesting that the formation of aqueous $CaCl_2$ solutions

9

1   does not necessarily require large amounts of chloride precursor gases or high

2   relative humidity.

3   It should be noted here that although the dust particles coated with chloride

4   were likely to be influenced by the formation of aqueous $CaCl_2$ solutions, most

5   of them had much lower Cl content than that expected for pure $CaCl_2$ (see Figure

6   2a), suggesting that Ca-containing compounds in the particles consisted partly

7   of unreacted carbonates or other salts. It is still unclear at the present time

8   whether other soluble salts coexisted with chloride in the same particles, and

9   further field and experimental studies on this topic are needed.

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Figure 1. (a) HYSPLIT backward trajectory analyses from the measurement site initialized on 21, 23, and 24 April 2007 at 06:00 UTC. Dots on each trajectory are plotted every 24 hours. (b) Time series of number concentrations of fine ($0.3 < D_p < 1.0$ µm) and coarse ($D_p > 1.0$ µm) particles measured at Kanazawa. Solid and dashed arrows indicate whether dust particles collected at the time preferentially contained chloride or not (see Figures 2a and 2b, respectively).

Figure 2. Relative atomic ratios of Ca:Cl:(Al + Si + Fe) and Ca:S:(Al + Si + Fe) for sea salt free-dust particles, and those of Na:S:Cl for sea salt particles. The compositions are from samples collected at 06:00-06:05 UTC (a) on 21 and 24 April 2007 (open and solid symbols, respectively) and (b) on 23 April 2007. Dashed lines are for Cl/Ca = 2 ratio; dashed-dotted lines are for S/Ca = 1 ratio; shaded regions are for $0.1 < Cl/Ca < 0.65$.

Figure 3. SEM/EDX images of a typical dust particle coated with chloride. The micrographs of the same particle are taken using 20 and 1.5 kV electron beams. Ni is a background peak from the mesh grid.

Figure 4. Equilibrium concentration of HCl as a function of water activity for the reaction $CaCO_3 + 2HCl$. Curves are plotted for pressures of 1000 and 700 hPa and for temperatures of 0, 10, 20, and 30°C. Each curve covers the range of RH higher than deliquescence RH for the hexahydrate of $CaCl_2$ at a given temperature. The calculations use the following parameters: Equilibrium constant for the reaction $CaCO_3 + 2HCl$ [*Kelly and Wexler*, 1995]; molality [*Kim and Seinfeld*, 1995] and activity coefficient [*Ananthaswamy and Atkinson*, 1985] of aqueous $CaCl_2$ solutions; CO_2 mixing ratios of 380 ppmv.

1   **Table 1.** Summary of the number of particles in Figure 2.

2

	Figure 2a	Figure 2b
Total analyzed particles	187	159
Mineral Dust (Sea Salt-free)	56	38
w Cl, w S	28	2
w Cl, w/o S	10	4
Sea Salt	97	93

3

(a)

50.0

Gobi Desert

Loess
Plateau

Sea of
Japan

Yellow
Sea

East
China
Sea

Kanazawa

● 21 April 2007
◆ 23 April 2007
□ 24 April 2007

Latitude (^{o}N)

40.0

30.0

20.0

90.0   105.0   120.0   135.0   150.0

Longitude (^{o}E)

(b)

300

200

100

0

N [0.3 < D_p < 1.0 um] (cm^{-3})

6

4

2

0

N [D_p > 1.0 um] (cm^{-3})

○ 0.3 < D_p < 1.0 um
■ D_p > 1.0 um

6   8   10   18   20   22   24   26

Day in April 2007 (UTC)
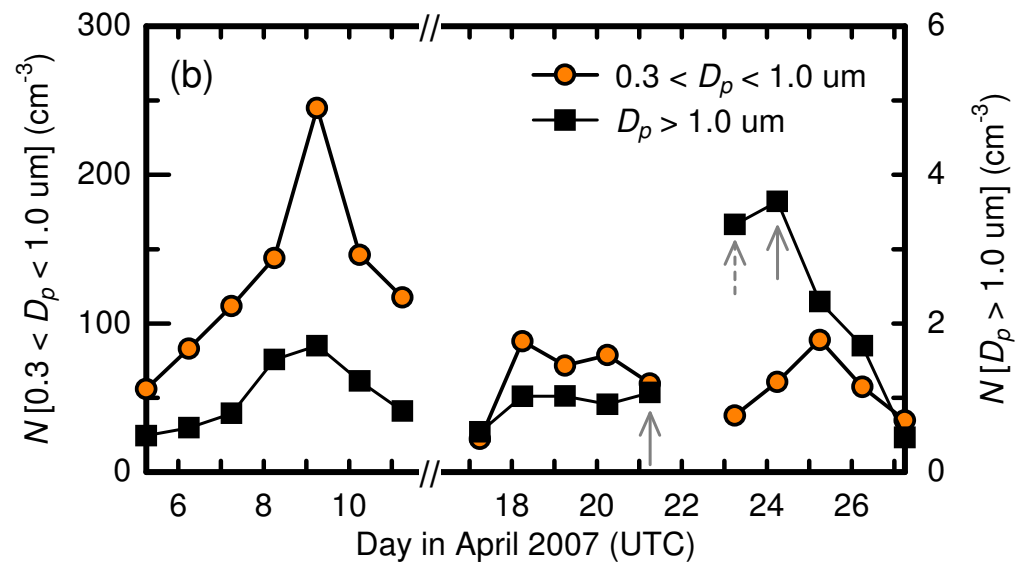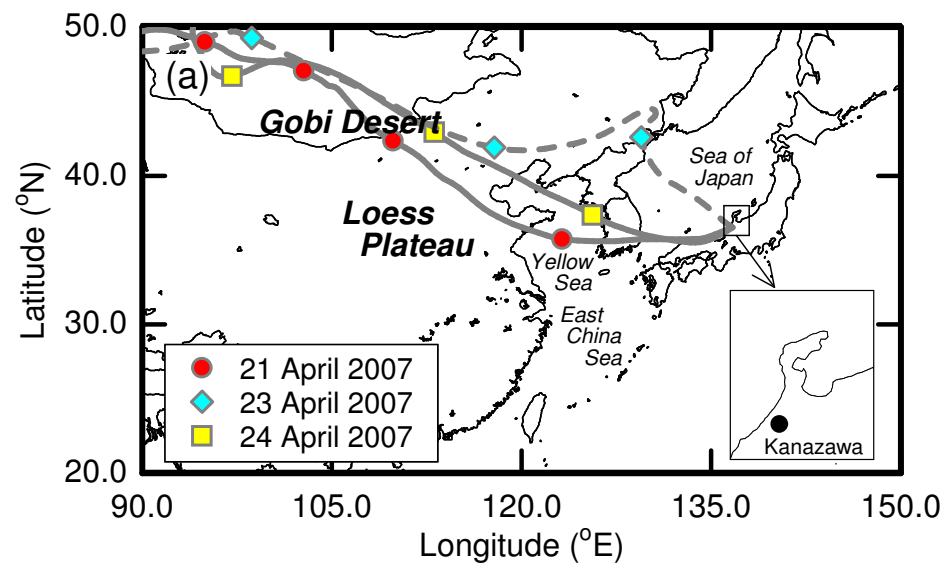
Mineral Dust (Sea Salt-free)

Sea Salt

(a)

Ca

Cl/Ca = 2
(CaCl$_2$)

Cl   Al + Si + Fe

Ca

S/Ca = 1
(CaSO$_4$)

S   Al + Si + Fe

Na

S   Cl

(b)

Ca

Cl   Al + Si + Fe

Ca

S   Al + Si + Fe

Na

20   80
40   60
60   40
80   20
20   40   60   80

S   Cl

20 kV

1.5 kV

5 um

5 um

Ni*

Mg

Al

Si

Cl

Ca

Ca

CPS

Mineral Dust
(Sea Salt-free)

X-ray energy (keV)

$CaCO_3$ (s) + 2HCl (g)
= $CaCl_2$ (aq) + H_2O (aq) + CO_2 (g)