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2 chemistry in the marine atmosphere

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1 **Abstract**

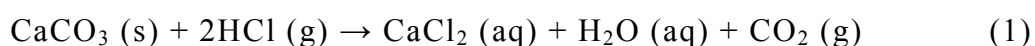
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3 Morphology and elemental compositions of individual dust particles were
4 investigated with the use of Asian dust samples collected at a site along the Sea
5 of Japan side of the archipelago. Our results indicate the preferential formation
6 of chloride in Ca-containing dust particles ($0.1 < \text{Cl}/\text{Ca} < 0.65$) 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 **1. Introduction**

2
3 Morphology and compositional changes of mineral dust particles in the
4 process of being transported in the atmosphere have an important impact on both
5 the Earth's albedo and climate. For example, heterogeneous chemistry of dust
6 particles with acidic gases such as NO_y (e.g., HNO₃, N₂O₅) and SO₂ will alter
7 the hygroscopic properties of the particles. So far, a number of both laboratory
8 and field studies have focused on the conversion of insoluble calcium carbonate
9 (CaCO₃) to highly soluble salts such as calcium nitrate (Ca(NO₃)₂) via
10 heterogeneous chemistry on dust surfaces [*Krueger et al.*, 2004; *Laskin et al.*,
11 2005; *Matsuki et al.*, 2005; *Hwang and Ro*, 2006]. Although many types of dust
12 particles are considered to modify the radiative properties of clouds by acting as
13 efficient heterogeneous ice nuclei (IN) [*DeMott et al.*, 2003; *Möhler et al.*,
14 2006], dust particles coated with soluble materials have the potential to act as
15 cloud condensation nuclei (CCN) at commonly found supersaturations [*Levin et*
16 *al.*, 1996; *Kelly et al.*, 2007].

17 Several field measurements have reported the formation of chloride in dust
18 particles, which they attribute not only to internal mixing processes of dust
19 particles with sea salt particles [*Zhang et al.*, 2003] but also to heterogeneous
20 chemistry of dust particles with chloride precursor gases [*Zhang and Iwasaka*,
21 2001; *Murphy et al.*, 2006; *Sullivan et al.*, 2007]. *Kelly and Wexler* [2005] have
22 proposed that CaCO₃ in dust particles could react with HCl in the atmosphere
23 via the following heterogeneous reaction pathway:



27 Nevertheless, there is an incomplete understanding of heterogeneous
28 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.

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.

1 The relative composition (normalized atomic percent) of elements with atomic
2 number (Z) ≥ 11 in each particle was calculated using ZAF (Z : Z -dependent
3 electron scattering, A : absorption, F : fluorescence) matrix correction. Since low
4 energy correction was not applied in the calculation, the relative composition of
5 Na tends to be somewhat overestimated [Zhang and Iwasaka, 2001; Zhang *et al.*,
6 2003]. In this study, the relative composition of low- Z elements such as C, N,
7 and O was not determined.

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

20

21 **3. Results**

22

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

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

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

24 The micrographs of a typical dust particle containing chloride were obtained
25 at different electron voltages in the high-vacuum SEM chamber (up to $\sim 10^{-3}$ Pa).
26 This approach is applied to the determination of the morphology and phase
27 changes of $\text{CaCO}_3/\text{Ca}(\text{NO}_3)_2$ particles [Laskin *et al.*, 2005]. As illustrated in
28 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

1 trace acidic gases (e.g., NO_y , SO_2 , HCl) could be removed from the atmosphere
2 by precipitation (up to 4.0 mm hour^{-1}) during the passage of the rain front, so
3 both dust and sea salt particles in the postfrontal air masses (i.e., just after the
4 passage of the rain front) could maintain their original composition without
5 chemical reactions during long-range transport. In contrast, sea salt particles
6 collected on 21 and 24 April 2007 became depleted of a greater or lesser degree
7 of chloride (see Figure 2a), indicating the release of HCl from the particles.
8 Since the chloride-depleted sea salt particles were found together with dust
9 particles coated with chloride, the release of HCl from sea salt might play a role
10 in the formation of chloride in dust particles.

11 *Sullivan et al.* [2007] have reported that the chlorine uptake by dust particles
12 can be attributed to the release of unusually large amounts of HCl from sea salt
13 particles, which are acidified by H_2SO_4 formed from the oxidation of volcanic
14 SO_2 . However, it is doubtful whether sea salt particles as presented in Figure 2a
15 had the potential to produce large amounts of HCl . This is because the aerosol
16 samplings were conducted under relatively unpolluted conditions by sulfur
17 compounds, and the degree of chloride depletion in the sea salt particles was not
18 so significant.

19 Under heavily polluted conditions by sulfur compounds, Cl will be driven
20 out of sea salt particles leading to enhanced HCl concentrations, but carbonate
21 components will also be driven out of dust particles and be replaced with
22 sulfate; hence, the formation of chloride in such dust particles should be hard to
23 take place. For instance, dust particles found in the samples of 9 April 2007
24 rarely contained chloride. Under relatively unpolluted conditions by sulfur
25 compounds, however, the replacement of carbonate with sulfate will be
26 suppressed. We consider that the observations on 21 and 24 April 2007 were
27 made under such conditions. So what is important for the formation of chloride
28 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 $\text{CaCO}_3 + 2\text{HCl}$ 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 $\text{CaCO}_3 + 2\text{HCl}$. (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 $\text{CaCO}_3 + 2\text{HCl}$ 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 $\text{CaCO}_3 + \text{HCl}$
28 under these conditions, suggesting that the formation of aqueous CaCl_2 solutions

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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2

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1 **Figure 1.** (a) HYSPLIT backward trajectory analyses from the measurement site
2 initialized on 21, 23, and 24 April 2007 at 06:00 UTC. Dots on each trajectory
3 are plotted every 24 hours. (b) Time series of number concentrations of fine (0.3
4 $< D_p < 1.0 \mu\text{m}$) and coarse ($D_p > 1.0 \mu\text{m}$) particles measured at Kanazawa. Solid
5 and dashed arrows indicate whether dust particles collected at the time
6 preferentially contained chloride or not (see Figures 2a and 2b, respectively).

7

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

14

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

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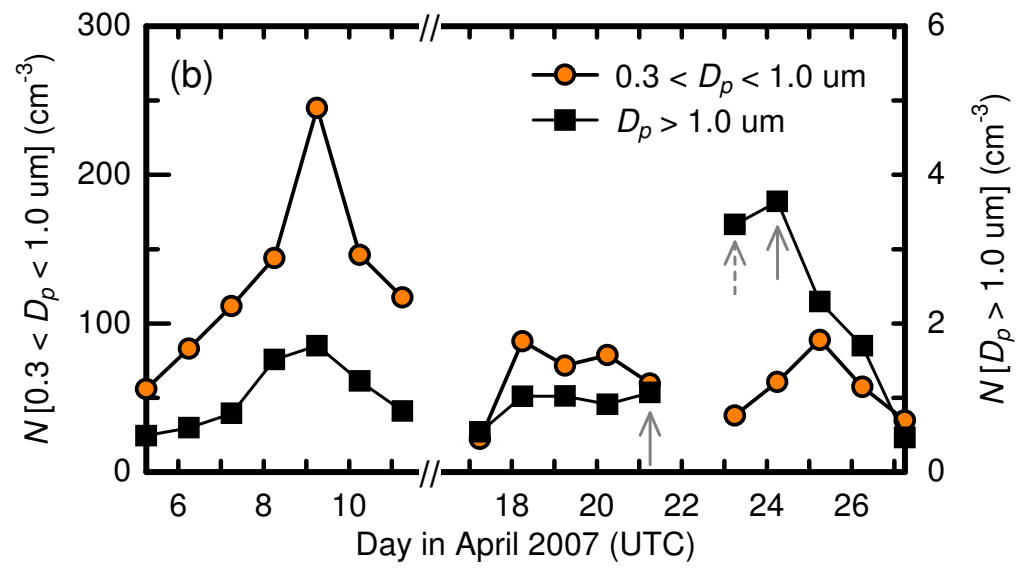
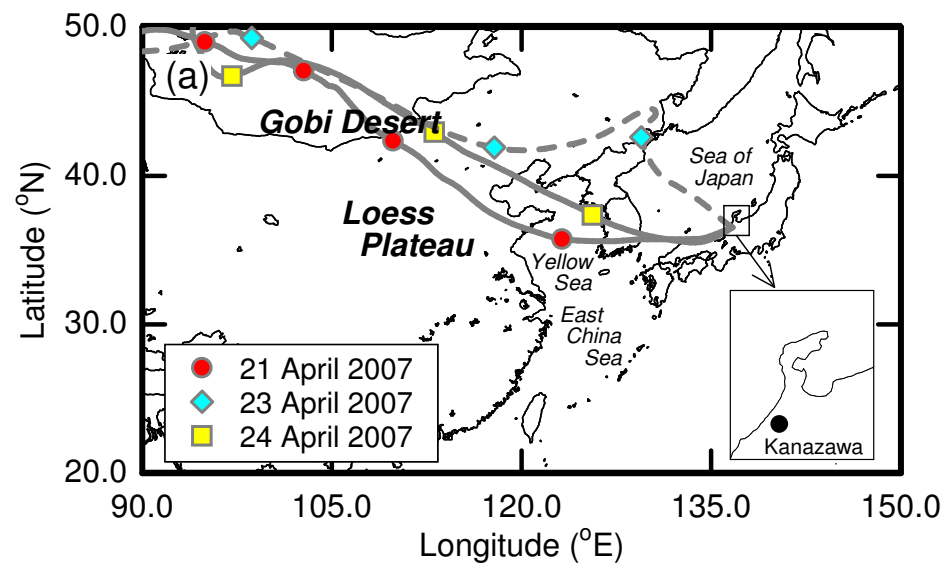
19 **Figure 4.** Equilibrium concentration of HCl as a function of water activity for
20 the reaction $\text{CaCO}_3 + 2\text{HCl}$. Curves are plotted for pressures of 1000 and 700
21 hPa and for temperatures of 0, 10, 20, and 30°C. Each curve covers the range of
22 RH higher than deliquescence RH for the hexahydrate of CaCl_2 at a given
23 temperature. The calculations use the following parameters: Equilibrium
24 constant for the reaction $\text{CaCO}_3 + 2\text{HCl}$ [Kelly and Wexler, 1995]; molality [Kim
25 and Seinfeld, 1995] and activity coefficient [Ananthaswamy and Atkinson, 1985]
26 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



Mineral Dust (Sea Salt-free)

Sea Salt

