The Effect of Continental Air Mass on the Modification of Individual Sea-Salt Particles Collected over the Coast and the Open Sea

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Abstract

Measurement of aerosol particles was performed over the North Pacific Ocean and the North Atlantic Ocean during two expeditions of the R/V Hakuho-Maru to investigate the modification of individual sea-salt particles. The analyzed results of individual particles with a scanning electron microscope and an energy dispersive X-ray spectrometer are as follows: (1) The Cl/Na mass ratios of square-shaped particles are nearly equal to the value of seawater (1.8), regardless of the particle size. (2) The Cl/Na ratios decrease with increasing the mass fraction of non sea-salt (excess) S in association with the change in shape on the collecting surface from square to circular or irregular. (3) From the relative mass ratios of Na, S and Cl, it is evident that the modified sea-salt particles contain not only Na_2SO_4 but also other compounds, for example NaNO_3 , as suggested by previous researchers. (4) The degree of modification over the sea is not dependent on the distance from the shore but on the transport time period, implying that the modification of sea-salt particles collected over the open seas is affected by the transport of the continental air mass. (5) It is found that the modification of the sea-salt particles is closely related to the concentration level of Aitken particles. There is no modification where the concentration of Aitken particles is less than about $400/\text{cm}^3$.

1. Introduction

The modification of sea-salt particles has been of interest in connection with the origin of atmospheric gaseous chlorine in the field of air chemistry (e.g., Oddie, 1959; Junge, 1956, 1963; Martens *et al.*, 1973; van de Vate *et al.*, 1978; Okada *et al.*, 1978, 1989).

Junge (1963) reviewed that the Cl/Na ratios in rainwater were always smaller than that in seawater. For example, Oddie (1959) found monthly averages of Cl/Na ratios in rainwater were 1.17 to 1.69 in Lerwick on the Shetland Islands. Junge (1963) explained that these results were due to the modification of NaCl reacting with H_2SO_4 and/or HNO_3 . He also reported that the S/Cl ratios decreased with increasing particle size (Junge, 1956).

Martens *et al.* (1973) studied aerosols collected by Andersen cascade impactors in Puerto Rico and the San Francisco Bay areas and analyzed Cl and Na by instrumental neutron activation analysis method. They found from the observational results that Cl loss increased with decreasing particle size. Okada

et al. (1978) performed simultaneous measurements of atmospheric gaseous chlorine and water-soluble material of aerosols at Owase and found that the Cl/Na ratios in aerosols were always lower than that in seawater. They suggested that the Cl deficiency (loss) was mainly due to the chemical reaction between the sea-salt particles and H_2SO_4 and HNO_3 originated from the gaseous materials such as SO_2 and NO_2 .

van de Vate *et al.* (1978) developed a battery-operated portable aerosol sampler for an electron microscopy, and applied it to the measurement of marine particles. The results of energy dispersive X-ray (EDX) analysis of the size-fractionated samples showed the S/Cl ratio increased with decreasing particle size. Also from the results of electron diffraction of individual particles they concluded that Cl^- was replaced by SO_4^{2-} in particles of the marine sub-micron size. Okada *et al.* (1989) investigated the modification of individual submicron sea-salt particles collected by an impactor in the coastal atmosphere. The EDX analysis showed that individual sea-salt particles were modified in the coastal atmosphere. They suggested that not only H_2SO_4 but

also HNO_3 were related on the modification of sea-salt particles.

There are only a few reports about the modification of sea-salt particles over the open sea (*e.g.*, Andreae *et al.*, 1986). Andreae *et al.* (1986) analyzed individual sea-salt particles collected over the equatorial Pacific Ocean between Ecuador and Hawaii. They found that a number of mixed-cation sulfates were commonly associated with sea-salt particles in the sample, collected relatively close to the coast of South America. They concluded that a cloud coalescence process might be responsible for the observed enrichment of non sea-salt sulfate in sea-salt particles.

The degree of modification will depend on the transport of pollutant from the land. Misaki and Takeuti (1970) studied the behavior of electric field and conductivity over the Pacific Ocean and the Sea of Japan, and discussed the extent of the land pollution. Their analyzed data showed that the conductivity, which is in inverse proportion to the concentration of aerosol particles in the atmosphere, was determined almost uniquely as a function of distance from the coastline when the weather was clear. Morita *et al.* (1973) investigated the extension of the land pollution to the oceanic atmosphere by the data obtained from nine expeditions over the Pacific Ocean and the East China Sea. They concluded that the age of the relevant air masses is the principal factor which controls the electrical state of the atmosphere over the oceans. They also concluded that the influence of air masses of age greater than about 60 hr on the conductivity and nucleus concentration seemed to be very small. Several researchers (*e.g.*, Misaki *et al.*, 1975; Ito *et al.*, 1986) investigated the life time of aerosol particles. Background aerosol was investigated by several researchers (*e.g.*, Junge and Jaenicke, 1971; Kojima and Sekikawa, 1974; Parungo *et al.*, 1986a). They observed anthropogenic air pollution from a continent over a remote ocean.

However, non sea-salt sulfate particles observed over the open sea are not always produced by anthropogenic SO_2 . The emission of biogenic dimethylsulfide ($(\text{CH}_3)_2\text{S}$, DMS) from the oceans to the atmosphere has been documented as a major natural source in the atmospheric sulfur budget (*e.g.*, Lovelock *et al.*, 1972; Hatakeyama *et al.*, 1985; Parungo *et al.*, 1986b; Andreae *et al.*, 1988). Laboratory experiments have shown that the DMS is an important precursor for SO_2 and methanesulfonic acid ($\text{CH}_3\text{SO}_2(\text{OH})$, MSA). The sea-salt particles may react with SO_2 , MSA, or non sea-salt sulfate due to the reaction of SO_2 over the open sea.

Moreover, the fraction of modified sea-salt particles observed over the open sea will depend on the size of the sea-salt particles because their production rate and the life time are dependent on their

size.

The purpose of this paper is to investigate the modification of individual sea-salt particles not only over the coast but also over the open sea by examining the elemental composition, the particle shape and size. We especially discuss the effect on the modification of continental air mass by associating it with the distance from the shore, the transport period, the concentration of Aitken particles and the radius of sea-salt particles.

2. Methods

The measurement and collection of aerosol particles were carried out on board the research vessel Hakuho-Maru during two expeditions, the KH89-T3 cruise (Fig. 1a) and the KH89-2 cruise (Fig. 1b).

In order to avoid the pollution from the ship itself, the sampling inlet for measuring the particle concentration was set on the upper deck at about 13 m above the sea surface and in the direction of 30 degrees left in front of the funnel of the ship. Air was drawn with a cleaner, whose flow rate was 180 l/min, through the sampling tube made of vinyl chloride of 18 mm in diameter and about 5 m long, to the No. 1 laboratory room behind the wheel house.

The aerosol particle concentration was continuously measured with a Pollak condensation nuclei counter (Pollak Counter), which determines the total number of particles larger than $0.001 \mu\text{m}$ (Kojima and Sekikawa, 1974). In continental air, the number of particles obtained by using this counter is practically identical with that smaller than $0.1 \mu\text{m}$ in radius, because of the relatively small concentration of larger particles (Junge, 1963). According to Junge's classification, these particles are called Aitken particles. As the existence of particles larger than $0.1 \mu\text{m}$ in radius can not be ignored in maritime air, it should be noticed that Aitken particles in this study contained a few of the particles larger than $0.1 \mu\text{m}$ in radius. Our Pollak Counter was compared with that made by Ito (1976, 1980) of the Meteorological Research Institute. Our results were in good agreement with those measured by Ito. The minimum countable concentration using our counter was 100 cm^{-3} .

The aerosol particles were collected directly on a carbon-covered nitrocellulose film supported on an electron microscopic grid by using a low-pressure cascade impactor (PIXE Int. Corp., Model I-1L) at the upper deck in front of a funnel of the ship. The flow rate of air was about 1 l/min and each aerosol sample was collected for 60 min except one sample (R4, 35 min). This impactor has seven stages but only two stages with 0.025 and $0.5 \mu\text{m}$ cutoff radius were used in this collection. The electron micrograph was obtained using a scanning electron microscope (SEM). The elemental compositions in individual particles larger than $0.1 \mu\text{m}$ in radius were

Fig. 1. Cruise chart and location of the sampling sites.
(a) KH89-T3 cruise and sampling site R1-R6.
(b) KH89-2 cruise and sampling site R7-R9.

analyzed with an energy dispersive X-ray spectrometer (EDX) (Horiba Co. Ltd., EMAX200). The elements whose atomic number is greater than or equal to that of Na were detected. In this study, according

to Okada *et al.* (1989), the particles which contain more than 30 % Na in the total mass of sea-salt elemental compositions (Na, Mg, S, Cl, K, Ca) were regarded as sea-salt particles. The sensitivity limit

Table 1. Sampling periods and locations used in this study.

Sample No.	TIME (GMT)	latitude	longitude	sea area	distance (km)*
R1	89/08/02 8:30 – 9:30	34°50'N	139°50'E	off Bousou	< 10
R2	89/08/06 23:30 – 0:30	34°26'N	142°46'E	off Bousou	250
R3	89/08/07 14:30 – 15:30	34°33'N	140°18'E	off Bousou	80
R4	89/08/07 22:25 – 23:00	35°15'N	139°47'E	off Bousou	< 10
R5	89/08/12 11:30 – 12:30	28°54'N	138°20'E	off Sikoku	530
R6	89/08/12 14:30 – 15:30	28°56'N	139°18'E	off Sikoku	540
R7	89/10/27 23:30 – 0:30	33°22'N	135°40'E	off Kii	20
R8	89/11/11 23:30 – 0:30	27°00'N	156°25'E	North Pacific	2700
R9	89/12/21 17:30 – 18:30	26°52'N	42°47'E	North Atlantic	2500

* the minimum distance from shore

of the EDX is defined by the minimum mass fraction (MMF) (Goldstein, 1979). In our analysis, the MMF values of Na, Mg, S, Cl, K, and Ca were smaller than 2, 12, 6, 3, 13, and 10 %, respectively.

The sampling periods and the locations used for this study are listed in Table 1. R1 to R6 and R7 to R9 are sample numbers during KH89-T3 and KH89-2 cruises, respectively. In this study, all samples were collected in the middle-latitude oceanic regions.

3. The modification of sea-salt particles over the sea

Figure 2 shows an electron micrograph of aerosol particles collected at R4 off the Bousou Peninsula on 7 August 1989. The X-ray energy spectra obtained from particles A–C are also indicated in the figure. Particle A which shows square-shaped features on the collecting surface contains Na, Mg, Si, S, Cl, K, Ca and Cu. The Cu peak in the spectra is due to cupreous grid used. The small Si peak is considered to originate from the evaporated carbon film used in the electron microscopy (*e.g.*, Okada *et al.*, 1990). The presence of Na and Cl at high intensity shows that these particles are sea-salt. Particles B and C show circular-shaped features and contain higher fraction of S than particle A. This relative relation suggests the modification of sea-salt particles with the exchange of S and Cl. The particles are classified into four groups according to their shapes; square-shaped (SQ), circular (CI), needle (NE) and irregular (IR), based on the analytical results of 101 sea-salt particles. The number of sea-salt particles examined and the averaged mass ratios of Cl/Na and S/Na are listed in Table 2.

Figure 3 shows the dependence of the Cl/Na mass ratios on the fraction of excess (non sea-salt) S (S(EX)) in total mass of sea-salt elemental compositions (Na, Mg, S, Cl, K, Ca). S(EX) is defined as $S(EX) = S(\text{measured}) - Na(\text{measured}) \times (S/Na)_{\text{seawater}}$. The Cl/Na ratios of particles analyzed with $S(EX) \cong 0$ are nearly equal to the value

of seawater (1.8), and the ratios decrease exponentially with increase of the value in the S(EX) fraction. Okada *et al.* (1989) reported the similar trend in the sea-salt particles collected over the coastal atmosphere. They also reported that there were extremely low Cl/Na ratios in spite of low values of S(EX), suggesting the contribution of HNO_3 to the modification of sea-salt particles. However, the fact was less evident in our data.

Marks in Fig. 3 indicate the types of particle shapes. There are few square particles when the Cl/Na ratios are less than unity. It can be said that the change in particle shape from square to circular or irregular should occur in association with the modification. Needle shaped particles were observed on both the modified and unmodified particles.

Okada *et al.* (1985) investigated the morphological features of individual particles collected in the remote oceanic atmosphere. They found that the cubic-shaped particles were sea-salt particles containing sulfate and they considered that the sulfate ions contained in them might originate from seawater. It was confirmed from our results that the square particles contained little non-sea-salt sulfur.

Cheng *et al.* (1988) investigated the evaporation of seawater drops in free fall in air. They showed that a majority of them at a relative humidity less than 60 % evaporated, became salt-saturated, and changed phase to produce hollow sea-salt particles. They also suggested that if the phase of the drops changed after collection on the stub, the circular spots would have been produced by the particles. In this study, the circular particles may come from the circular spots. If this fact is true, these circular particles would be collected as drops. On the other hand, the square-shaped or the irregular-shaped particles may be formed by the crystallization within drops.

Parungo *et al.* (1986b) discussed the states of crystallization within drops in detail. If the sea-salt components crystallize separately, the aggregates of loosely attached crystals of pure compounds

Fig. 2. Electron micrograph of sea-salt particles collected at station R4 with the cascade impactor during the period from 22:25 GMT to 23:00 GMT on 7 August 1989, and X-ray energy spectra of three particles (A to C). Cu in the spectra is due to the Cu grid used in the present study.

are formed by drying. The aggregates subsequently shatter in air to produce individual pure crystals. However, if the drops evaporate rapidly or if other factors which prevent crystallization in drops exist, the mixtures of compounds are formed in individual particles and the shattering does not occur.

Though not shown here, from the two-dimensional distribution of the sea-salt elemental compositions, it is shown that the mixing state of the modified particles is not the aggregation of individual pure substances but the uniform mixture of substances in individual particles. As listed in Table 3, the relative humidity of the sampling air was 72–94 %. It is suggested that the sea-salt particles were usually suspended in air as drops and these particles were crystallized rapidly during the sampling. Anyway,

the value of the relative humidity where the phase transition arises for circular particles may be lower than that for other shaped particles.

Figure 4a shows the relative mass ratios of Na, S and Cl for all data used in this study. The cross mark close to the Na–Cl line indicates the value in seawater. The square-shaped particles are present near this mark. Two marks (+) on the line between Na–Cl and Na–S indicate the ratios for NaCl and Na_2SO_4 , respectively. If the sea-salt particles consist of only NaCl and Na_2SO_4 , the values for these particles should scatter around the broken line. Measured data are distributed on the upper side of this line, indicating that the sea-salt particles contain other compounds besides NaCl and Na_2SO_4 , for example NaNO_3 as already suggested by other

Table 2. The number of sea-salt particles examined and averaged mass ratios of Cl/Na and S/Na. Morphological features of sea-salt particles are also listed; square-shaped (SQ), circular (CI), needle (NE) and irregular (IR).

Sample No.	No. of particles					Mass ratio	
	total	SQ	CI	IR	NE	Cl/Na	S/Na
R9	9	9	0	0	0	1.7	0.1
R2	9	9	0	0	0	1.6	0.1
R8	18	16	0	0	2	1.5	0.1
R1	11	11	0	0	0	1.5	0.2
R5	13	0	10	3	0	0.9	0.2
R7	17	8	5	4	0	0.6	0.2
R4	10	3	7	0	0	0.6	0.3
R6	9	0	6	3	0	0.1	0.5
R3	5	0	1	2	2	0.0	0.9
SW*						1.80	0.08
total	101	56	29	12	4		

* values in seawater

workers (*e.g.* Junge, 1963; Okada *et al.*, 1989). Unfortunately, our analysis system could not detect nitrogen.

The average ratios at sampling sites are plotted with figures corresponding to the sampling sites R1 to R9 in Fig. 4b and listed in Table 2. The degree of modification is different according to the sampling sites. The order of the Cl/Na ratio was R9, R2, R8, R1, R5, R7, R4, R6 and R3.

4. Effect of continental air mass on the modification

It was shown that the degree of modification differed among different sampling sites. The degree of modification over the sea depends on the production rate of sea-salt particles and the amount of pollutant, for example SO₂ or sulfate particles. The production rate and the size of sea-salt particles de-

Fig. 3. Cl/Na ratio of sea-salt particles as a function of fraction of excess S. Marks correspond to particle shape.

pend on the wind force (*e.g.*, Kojima and Sekikawa, 1974) and the life time of sea-salt particles depends on their size. Tables 2 and 3 show no relationship between the degree of modification and the wind speed.

The pollutant will be transported from the land. During transport, it will be deposited into the sea and diffuse toward the upper air. Moreover, the modified sea-salt particles are also transported and their life time is dependent on their radius. In order to investigate the degree of modification due to the transport of the continental pollutant, the Cl/Na ratios are associated with the minimum distance from the shore, the transport period, the concentration of Aitken particles and the particle radius of sea-salt. For example, we show the relative mass ratios of Na, S and Cl at R5 and R9 in Figs. 5a and 5b, respectively.

The minimum distance at a sampling location was

Table 3. Weather elements, and the concentration of aerosol particles at the sampling locations.

Sample No.	temp. (°C)	r.h. (%)	w.s. (m/s)	w.d.	A.p. (/cm ³)	transport period (day)
R1	26.9	—	5.3	E	<100	8
R2	25.3	94	8.2	S	<100	6<
R3	26.5	86	8.9	SW	1426	2.5
R4	26.4	79	6.0	SW	4942	2
R5	27.1	79	2.7	SE	1441	2.5 (7)
R6	26.8	80	4.1	SE	446	2.5 (7)
R7	23.2	81	9.9	NE	938	0.2 (4)
R8	24.8	78	12.6	S	336*	10<
R9	23.2	72	5.1	SW	328	3.5

* data at 4:00 11/12

Fig. 4. Relative mass ratios of Na, S and Cl for all data (a), and the average ratios of each sampling site are plotted with figures corresponding to sampling sites R1 to R9 (b).

Fig. 5. Relative mass ratios of Na, S and Cl, and air mass back-trajectories for R5 (a) and R9 (b). The pressure profiles are shown in the lower portions.

determined simply by the distance from the ship to the nearest shore. For example, the distance at R5 was determined on 530 km by the distance from the ship to Kii Peninsula (Fig. 5a). The obtained distances are listed in Tables 1.

The transport period was obtained from the analyzed results of air mass trajectory. The isentropic backward-trajectory was originally calculated every 3 hr by using the daily standard pressure level data belonging to Long-Range Forecast Division, the Japan Meteorological Agency (Kumakura *et al.*, 1990). For example, we show the trajectories at R5

and R9 in Figs. 5a and 5b, respectively. The pressure profiles are also shown in the lower portions of the figures. The trajectory in Fig. 5b shows that the air mass departed from the shore at 900 GMT 18 Dec. and arrived at R9 at 1800 GMT 21 Dec. so that the air was transported for 3.5 days. However, Fig. 5a shows that the air mass at R5 did not depart from the shore and got near the shore 2.5 days before. This trajectory was drifting around the sampling location so that data for this trajectory were not very reliable. The trajectory of air mass at R6 was similar to that at R5. Radon concentrations at

Fig. 6. The relationship between the Cl/Na ratios and distance from shore (a), transport period (b), Aitken particle concentrations (c) and particle radius of sea-salt (d).

R5 and R6, which were obtained by assuming the decay equilibrium, were higher than that at the center of the Pacific Ocean. Therefore, we consider that these air masses departed from the shore 2.5 days before. The transport periods obtained are listed in Table 3.

Figure 6a shows the dependence of the Cl/Na ratios on the minimum distance. The sea-salt particles collected at R1 (<10 km), R2 (250 km), R8 (2700 km) and R9 (2500 km) are little modified, while those at R5 and R6 are rather modified in spite of the distance of over 500 km. These results suggest that the degree of modification of sea-salt particles is not influenced by the distance from the coast. But this does not mean the modification is not influenced by the continental air mass. Halter and Robinson (1977) measured Aitken particle concentration over the Eastern Pacific Ocean and reported that the highest concentration, over $4,000/cm^3$, were measured in the northeast trade wind belt at about 700 km off Central America.

Figure 6b shows the relation between the Cl/Na ratios and the transport periods. When the transport period is shorter than 3 days, the ratios are scattered. On the other hand, when the transport period is longer than 3 days, the ratios are nearly equal to the value of seawater. These relationships are similar to the relationship between the concentration of Aitken particles and the transport period obtained by Morita *et al.* (1973). Their threshold value was 60 hr (2.5 days). It seems that our value of 3 days is in good agreement with their value. But we should note that the air mass at R9 was a special case. The pressure profiles of trajectories in Fig. 5b show that the air sampled at R9 was transported from the free troposphere (ca. 500 mb) over America, while the air at other sites, e.g. R5 shown in Fig. 5a, was transported within the marine boundary layer. Since the air mass in the free troposphere is clean, the Aitken particle concentration at R9 was low in spite of a short transport period of 3.5 days (Table 3). If we ignore the data at R9, we can not ac-

curately determine the threshold period. This value is between 2.5 to 6 days and perhaps longer than 3 days. Anyway, the sea-salt particles are not modified if the transport period is longer than 6 days.

The relation between the Cl/Na ratios and Aitken particle concentration in Fig. 6c shows that the ratios keep the value of seawater when the Aitken particle concentration is lower than a certain value. This threshold value is considered to be between 336(R8) to 446(R6)/cm³, which are practically total concentration measured with the Pollak Counter. The values greater than *ca.* 400/cm³ are due to an influx of continental air so that the ratio of modified particles show scattered values. This threshold value is almost equal to the background concentration (Kojima and Sekikawa, 1974) and four thousandths of the continental value, *ca.* 100,000/cm³ in Tokyo in winter (Miura and Sekikawa, 1990).

Figure 6d shows the dependence of the Cl/Na ratios on particle radius of sea-salt. The size indicated in this paper is apparent size on the collecting surface. The ratios for square-shaped particles are close to 1.8 and do not depend on the particle size. On the other hand, the low ratios are especially found in particles of small size range whose shapes are circular or irregular. Moreover, the larger particles are little modified because their life time is shorter. The smaller sea-salt particles have longer life time so that they have chance to react with the pollutant and to be modified more than the larger sea-salt particles.

The sea-salt particles may have been transported over the ocean after the modification at the continent or the coastal region, and/or may have been generated and modified during the transport. In the latter case, the sea-salt particles may have reacted with MSA or SO₂ due to the reaction of DMS. Our results show that (1) modified sea-salt particles are not prevalent in the long-range transported air mass and (2) there are no extremely modified larger sea-salt particles. These results mean that the modification of sea-salt particles collected over the open seas is affected by the transport of the continental air mass. As for our samples, it seems that the sea-salt particles hardly react with MSA or SO₂ due to the reaction of DMS, but it may be limited to the sample in the middle-latitude oceanic regions. A more detailed study on the modification of sea-salt particles should be carried out by examining a large number of particles in the future.

5. Conclusions

It was found that the individual sea-salt particles changed in shape from square to circular or irregular with increasing the degree of modification.

In this study it was confirmed that: (1) The Cl/Na ratios for square shaped particles were nearly equal to the value of seawater. (2) The ratios decreased with increasing the mass fraction of non

sea-salt. (3) The sea-salt particles contained other compounds besides NaCl and Na₂SO₄, for example NaNO₃.

The degree of modification over the sea is not dependent on the distance from the shore but on the transport time period. It means that the modification of sea-salt particles collected over the open seas is affected by the transport of the continental air mass. It is found that the modification of the sea-salt particles is closely related to the concentration level of Aitken particles. There is no modification where the concentration of Aitken particles is less than about 400/cm³.

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沿岸及び外洋で捕集した個々の海塩粒子の変質に与える大陸性気塊の影響 三浦和彦・熊倉俊郎・関川俊男

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白鳳丸で捕集した個々の海塩粒子を走査型電子顕微鏡とエネルギー分散型 X 線分析器で分析し、変質の程度を捕集場所別に調べた。

(1) 正方形をした粒子の Cl/Na 質量比は、粒径によらず海水中の比 1.8 に近かった。(2) 非海塩成分の S が増加するにつれ、Cl/Na の値は小さくなり、円形・不規則形状の粒子が多くなった。(3) Na, Cl, S の相対質量比を三角ダイアグラムで表わすと、解析した値は NaCl–Na₂SO₄ の混合ラインより上に分布し、NaCl の変質は Na₂SO₄ のほかに、他の化合物たとえば NaNO₃ に関与していることを示唆する結果が得られた。(5) 気塊の輸送時間、エアロゾル粒子濃度との比較から、海塩粒子の変質は捕集場所が大陸の影響をある程度以上受けているときに起こることがわかった。このしきい値は、Aitken 粒子濃度で 400 個/cm³ だった。