Title	The rates of sea salt sulfatization in the atmosphere and surface snow of inland Antarctica
Author(s)	Iizuka, Yoshinori; Tsuchimoto, Akira; Hoshina, Yu et al.
Citation	Journal of Geophysical Research, Atmospheres, 117, D04308 https://doi.org/10.1029/2011JD016378
Issue Date	2012-02-28
Doc URL	https://hdl.handle.net/2115/49886
Rights	Copyright 2012 by the American Geophysical Union.
Type	journal article
File Information	JGR117_D04308.pdf

The rates of sea salt sulfatization in the atmosphere and surface snow of inland Antarctica

Yoshinori Iizuka,[1] Akira Tsuchimoto,[1] Yu Hoshina,[2] Toshimitsu Sakurai,[1] Margareta Hansson,[3] Torbjörn Karlin,[3] Koji Fujita,[2] Fumio Nakazawa,[4] Hideaki Motoyama,[4] and Shuji Fujita[4]

[1] Most of the aerosol particles present in the surface snow and ice of inland Antarctica come from primary sea salt (sodium chloride) and marine biological activity (methansulfonic and sulfuric acids). Melted water from surface snow, firn, and Holocene ice contains mainly sodium, chloride, and sulfate ions. Although it is well known that sea salt aerosols react rapidly with sulfuric acid, a process known as sulfatization, it is not known when this process takes place. In this research we undertake to measure the proportion of sea salt aerosols that undergo sulfatization in the atmosphere and surface snow, as opposed to deeper ice, in order to understand the suitability of sea salt aerosols as a proxy for past climates in deep ice cores. We directly measure the sulfatization rates in recently fallen snow (0–4 m in depth) collected at the Dome Fuji station, using X-ray dispersion spectroscopy to determine the constituent elements of soluble particles and computing the molar ratios of sodium chloride and sodium sulfate. We estimate that about 90% of the initial sea salt aerosols sulfatize as they are taken up by precipitation over Dome Fuji or in the snowpack within one year after being deposited on the ice sheet.

1. Introduction

[2] Atmospheric aerosol particles in the free troposphere have a strong influence on direct and indirect radiation effects in the Earth's atmosphere [*Andreae*, 1995]. Some aerosol particles are formed by the disintegration of bulk material on the Earth's surface (e.g., sea salt and dust), while others are produced by chemical reactions (scavenging and loss of gases, aqueous phase reactions) in the atmosphere. The latter are known as secondary aerosols.

[3] In the present (Holocene) climate, the most common aerosols present in inland Antarctic ice and snow come from sea salt (sodium chloride) and marine biological activity (methansulfonic and sulfuric acids) in the Southern Ocean [e.g., *Legrand et al.*, 1988]. Both of these aerosols are soluble, so melted samples of surface snow, firn, and ice from inland Antarctica contain mainly sodium, chloride, and sulfate ions [e.g., *Legrand et al.*, 1988].

[4] It is well known that sea salt aerosols can undergo a number of rapid chemical reactions as they are transported to inland Antarctica. Due to the large amount of sulfuric acid in the Antarctic atmosphere, the most important reaction during the Holocene and similar climates is sulfatization [e.g., *Legrand et al.*, 1988; *Delmas et al.*, 2003]:

$$H_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2HCl$$
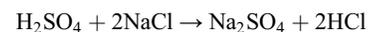
Ultimately, it is this reaction that determines the molar ratio of sodium chloride to sodium sulfate observed in snow, firn, and ice.

[5] Since the sea salt and biological acids are typically transported over long distances (about 1000 km from the Southern Ocean to inland Antarctica), and since few aerosols are added from the Antarctic ice sheet during this journey, the chemical compositions and relative abundances of aerosols present in the inland snow of Antarctica provide good constraints on the rate of sulfatization in the atmosphere, which is currently unknown.

[6] In the present Antarctic atmosphere, the ratio of sodium chloride to sodium sulfate is highest during the winter. The reason is clear: in winter, sea salt aerosols (sodium and chloride ions) are at their maximum concentrations because cyclones frequently carry seawater from the Antarctic sea to the inland ice sheet [*Delmas et al.*, 2003]. The molar ratio is lowest in summer, when marine biological activity produces a great deal of sulfuric acid,

[1]Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan.
[2]Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan.
[3]Department of Physical Geography and Quaternary Geology, Stockholm University, Stockholm, Sweden.
[4]National Institute of Polar Research, Tokyo, Japan.

which passes into the atmosphere and there promotes sulfatization [*Delmas et al.*, 2003]. Thus, there is a well-documented seasonal variation in the relative abundances of aerosols and their reaction products.

[7] Long-term variations in the Antarctic climate also have an impact. The ion concentration profiles of deep ice cores can be used to reconstruct the history of aerosols over the past several hundred thousand years, a period that includes several glacial cycles. Long-term paleoclimate studies of Antarctica have been carried out on ice cores from Byrd [e.g., *Johnsen et al.*, 1972], Vostok [e.g., *Petit et al.*, 1999], Dome Fuji [e.g., *Watanabe et al.*, 2003], EPICA DML [*EPICA Community Members*, 2006], and EPICA Dome C [*EPICA Community Members*, 2004].

[8] Some recent studies have proposed that chemical reactions such as sulfatization may not just occur in the atmosphere during transport to inland Antarctica, but also in the surface snow and firn [*Wagnon et al.*, 1999; *Röthlisberger et al.*, 2003; *Iizuka et al.*, 2006]. The time scale of this process, however, is unknown. If sea salt sulfatization continues in the ice sheet for a long time after the snow is deposited, and accounts for a large fraction of the total reaction rate, then the value of these chemical compounds as proxies for past atmospheric aerosols would be diminished. It is therefore interesting to find out exactly how much sea salt sulfatizes in the atmosphere during transportation, how much of it sulfatizes during precipitation and in recently fallen snow, and how much of it sulfatizes deep in the ice layer.

[9] Many studies have tried to constrain the proportions of compounds affected by this reaction by measuring the ratio of Cl^- to Na^+ [e.g., *Legrand et al.*, 1988; *Delmas et al.*, 2003; *Mulvaney and Wolff*, 1994; *Udisti et al.*, 2004]. These studies may work with melted ice samples, aerosols collected from the atmosphere, or freshly fallen snow.

[10] In the Dome Fuji region of our previous study [*Iizuka et al.*, 2004], Na^+ concentrations in freshly precipitated snow from 1995 to 1997 were largest (1.57 μmol/l on average) during the winter and spring (from July to September) and smallest (0.20 μmol/l) during the summer (from December to February). Cl^- concentrations in fresh snow, on the other hand, were slightly higher during winter (2.77 μmol/l) than during summer (2.50 μmol/l). Even during winter, the Cl^- concentration at Dome Fuji is almost twice that of Na^+.

[11] *Hara et al.* [2004] found the same seasonal trend of Na^+ and Cl^- concentrations in aerosols collected from the atmosphere at Dome Fuji during 1998. The fact that Cl^-/Na^+ is higher during summer can be attributed to the transportation of gaseous HCl, which is a product of sulfatization, in the atmosphere [e.g., *Legrand et al.*, 1988]. Some Na^+ is removed from the Na_2SO_4 produced during atmospheric transportation over the Antarctic Ocean. These results suggest that ion measurements of aerosols captured in the atmosphere can reflect the amount of sulfatization that occurs during transportation.

[12] By comparing ion concentrations on the ground with those detected in the atmosphere, we reach some interesting results. Non-sea-salt (nss) SO_4^{2-} concentrations in fresh snow at Dome Fuji are smallest in summer (0.74 μmol/l) and largest in winter (1.11 μmol/l) from 1995 to 1997 [*Iizuka et al.*, 2004]. In atmospheric aerosols, however, K. Hara *et al.* found that nss-SO_4^{2-} concentrations were highest

during summer at the same location in 1998 (personal communication, 2011; their Na^+ and Cl^- concentrations are published in the work by *Hara et al.* [2004]). *Jourdain et al.* [2008] also found a summer maximum for the nss-SO_4^{2-} concentration in atmospheric aerosols over Dome C (another dome of east Antarctica).

[13] Apparently, the fresh snow at Dome Fuji has a seasonal pattern of nss-SO_4^{2-} concentrations opposite to that of the atmospheric aerosols. However, the SO_4^{2-} concentration in fresh snow is greater than the Na^+ concentration during all seasons. Even in winter, there is always an excess of sulfate ions compared to sea salt (sodium ions). Dome Fuji snow has very few anthropogenic sulfate aerosols; it is known that the aerosols in Antarctic snow come mainly from the Antarctic Ocean and high-latitude regions of the southern continents. Furthermore, very little change in the sulfate ion concentration has been observed over the past 150 yrs; the level today is comparable with long-term estimates from the Holocene period [*Iizuka et al.*, 2004; *Igarashi et al.*, 2011]. Therefore, the patterns just described provide evidence for sulfatization during precipitation and deposition.

[14] However, because the ion concentrations lack information on the original chemical compounds of the aerosols, these data are insufficient to quantify the rate of sulfatization during this phase. We also have little knowledge of the reactions that take place in the snow and firn of inland Antarctica.

[15] Recently, we developed a sublimation method capable of collecting several hundreds of nonvolatile particles from a small ice sample at temperatures below −45°C [*Iizuka et al.*, 2009]. The same system can be applied to surface snow and firn. Using scanning electron microscopy and energy dispersion X-ray spectrometry (SEM-EDS), we can determine the constituent elements of these particles and also classify them as insoluble or soluble [*Iizuka et al.*, 2009]. In this paper, we collect and identify soluble, nonvolatile particles from surface (0–4 m) snow at the Dome Fuji station, and calculated the masses of sodium sulfate and sodium chloride in surface snow. These measurements allow us to quantify the amount of sea salt that sulfatized during precipitation over Dome Fuji and in the surface snow, as opposed to during transportation through the atmosphere. Our result confirms the reliability of ice core aerosols as indicators of past atmospheric chemistry.

2. Experimental Method

[16] From 10 to 12 December 2007, the Japanese-Swedish Antarctic Traverse Expedition (JASE) cut blocks of surface snow at varying depths from the sides of a snow pit at the Dome Fuji (DF) Station. The DF Station is located at one of the highest points of central Antarctica (77.2S, 39.4E), 3810 m above sea level. Each snow block is a rectangular solid measuring about 200 × 200 × 500 (depth) mm. Eight such blocks were cut in a vertical column, the lowest extending to a maximum depth of 4.0 m. The blocks were transported in the frozen state to a cold laboratory at the Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan.

[17] At the laboratory, they were preserved at temperatures not higher than −45°C, below the eutectic temperatures of major salts [*Ohno et al.*, 2005]. We took column-shaped

samples (diameter 8 mm and length 30 mm) by piercing the block with a pre-cleaned stainless steel pipe. To avoid contamination from the surface of the block, we removed the first 10 mm of snow. The remaining sample (8 mm by 20 mm) was placed inside a cylindrical sublimation chamber, its circular face resting on a polycarbonate membrane filter with pores 0.45 μm in diameter.

[18] The sublimation chamber is a stainless steel pipe with inside diameter 8 mm and length 100 mm. The samples were treated using a laminar flow bench (class 100). We channeled clean, dry air with a dew point of $-65°C$ through the pipe at a rate of 15 l/min over a period of about 70 h, sufficient to completely sublimate the ice. The air contained no oil or solid particles more than 0.03 μm in diameter.

[19] After sublimation, the sample's nonvolatile particles remain on the membrane. We measured the constituent elements and surface areas of these particles for a total of 20 snow samples: six segments of about 15 mm depth resolution, ranging from the surface to 0.1 m in depth, and fourteen segments of about 0.30 m depth resolution, ranging from 0.1 to 4 m in depth. We avoid the depth ranges 1.0 to 1.3 m and 3.3 to 3.6 m, because these snow layers might contain volcanic impurities. (Such impurities have been detected by ordinary soluble ion analysis [see *Hoshina*, 2010].) We also analyzed a section of firn taken from a depth of 18 m at the Dome Fuji station, which was drilled in 1999. The sublimation system is described in detail by *Iizuka et al.* [2009].

[20] Soluble sodium, chloride, and sulfate ion concentrations at the same depths as the snow blocks were measured by ion chromatography (Dionex 500) following the method described by *Hoshina* [2010]. This apparatus measures the concentrations of soluble ions with a precision better than 5%.

3. EDS Data Reliability

[21] The nonvolatile particles on the filter were analyzed for constituent elements using a JSM-6360LV (JEOL) SEM (scanning electron microscope) and a JED2201 (JEOL) EDS (energy dispersive X-ray spectrometry) system. The accelerating voltage was 20 keV, high enough for the electron beam to penetrate particles several μm in diameter. The X-ray spectrum of each particle was measured for a period of about 60 s. Each snow sample yielded at least 180 particles more than 0.4 μm in diameter, whose constituent elements could be determined by SEM-EDS.

[22] We calculate the total mass of Na, S, and Cl by assuming that each particle is a sphere whose radius is calculated from its cross-sectional area on the SEM image. That is, the particle volume V (μm^3) is estimated as

$$R = (CA/\pi)^{1/2}$$

$$V = 4/3\,\pi R^3$$

where CA and R are the cross-sectional area (μm^2) and inferred radius (μm) respectively. The particle mass m (μg) is

$$m = \rho V \times 10^{-9}$$

where the density ρ is assumed to be 2500 kg·m^{-3} for insoluble dust [*Petit et al.*, 1999].

[23] EDS can measure an "atomicity ratio" for each detected element by comparing the signal of its peak to the total signal due to all elements (the range is therefore 0 to 1). For example, the sodium mass m_{Na} (μg) is expressed as

$$m_{Na} = W_{Na}A_{Na}(\Sigma W_i A_i)^{-1} \times m,$$

where m is the total mass of the particle. W and A are the atomic weight and atomicity ratio respectively. The subscript i refers to the eight major detected elements: O, Si, Al, S, Cl, Na, Mg, and Ca (see Appendix A and section 4). We assume that all particles consist almost entirely of these eight elements, so that $\Sigma A_i = 1$.

[24] We checked the reproducibility of the mass measurement for a single particle by the following method.

1. We measured the eight atomicity ratios 20 times for a single particle selected at random.

2. We calculated the coefficient of variation (CV) for each atomicity ratio, based on the average values and standard deviations of these 20 measurements. For example, the standard deviation of the Na atomicity ratio in this data set is 7.2, while the average atomicity ratio is 17.9. The CV of the Na atomicity ratio is therefore 0.40. The CVs of S and Cl were 0.39 and 0.45 respectively.

3. Because the eight elements had similar CVs in step 2, we took their average: 0.40. Henceforth, we assume that any individual atomicity ratio measurement follows a normal distribution with a CV equal to 0.40. The mean atomicity ratio measured over N particles therefore has the relative uncertainty $CV_N = \frac{0.40}{\sqrt{N}}$. We repeated the above procedure with several other particles, obtaining similar results in each case.

[25] In the analysis to follow, we will assume that the masses and moles of sodium sulfate and sodium chloride can be inferred directly from the elemental masses, which are directly proportional to the atomicity ratios measured in the X-ray spectra. In the case of sodium sulfate, for example, we obtain an uncertainty based on the average CV for an atomicity ratio and the number of particles (N_{NaS}) for which both Na and S are detected: $CV_{N_{NaS}} = \frac{0.40}{\sqrt{N_{NaS}}}$. When calculating the mass ratio or molar ratio of sodium sulfate to sodium chloride, the measurement which we shall use to constrain sulfatization rates, the relative uncertainty is expressed as

$$CV_{ratio} = 0.40\left(\frac{1}{N_{NaS}} + \frac{1}{N_{NaCl}}\right)^{\frac{1}{2}},$$

following the standard rule of error propagation.

[26] The maximum value of CV_{ratio} is 0.234, at the depth of 2.24 m, and its average value over all depths is 0.123. The relative uncertainties given by this formula depend only on the number of particles detected for each species, so vary little with depth. The standard deviation of CV_{ratio} (for the ratio of sodium sulfate to sodium chloride) over all the samples is only 0.032, so in most cases the ratios reported in section 4 can be taken as having uncertainties in the range of 10% to 15%.

[27] In this manuscript, we calculate elemental masses in terms of the mass ratios on a single particle. Thus, any biases
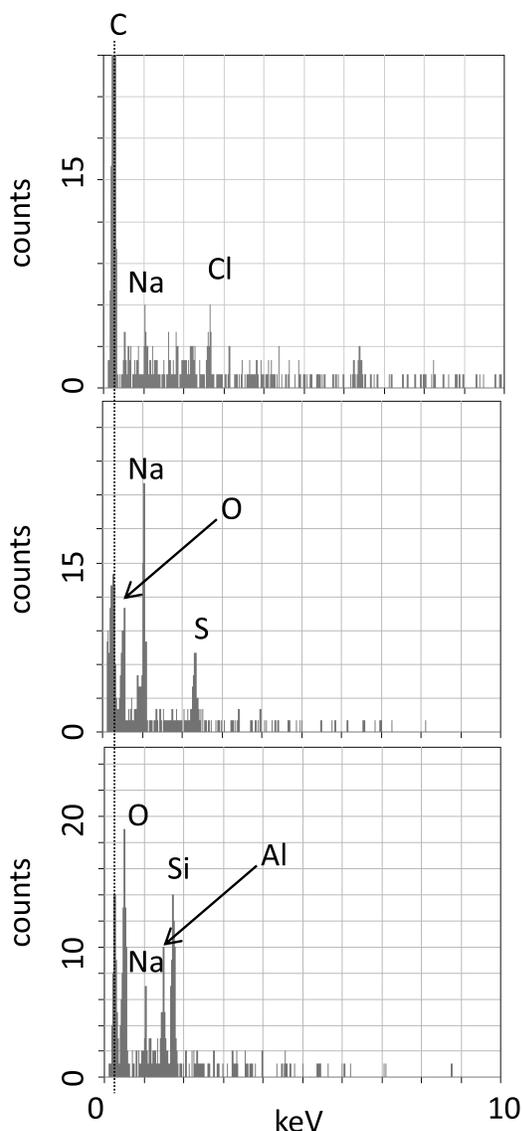
Figure 1. From top to bottom: typical electron diffraction spectra of nonvolatile particles containing sodium and chorine (sodium chloride), sodium and sulfur (sodium sulfate), and sodium and silicon (insoluble sodium). The carbon signal comes from the filter.

related to the approximation of a uniform density sphere are eliminated in the course of calculation.

4. Results and Discussion

4.1. The Soluble Elements and Related Ion Concentrations

[28] Among the nonvolatile particles found at depths from 0.01 m to 3.85 m, we detected eight major elements: O, Si, Al, S, Cl, Na, Mg, and Ca. We also observed C, Cr, and Fe on a few occasions, but interpret these peaks as artifacts from the membrane filter (C), sample mounting (Cr), and the stainless steel of the sublimation system (Fe). Other elements are only rarely detected. Figure 1 shows three EDS results from surface snow at 4 m depth. Many particles have the pairs (S, Na) and (Cl, Na). In this paper we focus on

particles containing Cl, S, and Na, especially the two pairs just mentioned. As described in the Appendix, after separating soluble and insoluble particles (for a complete description of this experimental method [see *Iizuka et al.*, 2009]), we found that almost all (more than 99%) particles containing S or Cl were soluble. Also, it is important to note that when separating the nonvolatile particles containing Na into soluble and insoluble types, only those which also contained Cl or S were soluble. Therefore, we keep separate counts of Na-containing particles (total-Na) and soluble particles containing both Na and either Cl or S (soluble-Na).

[29] Figure 2 plots the fraction of nonvolatile particles containing Cl, S, and Na (total-Na), as well as the fraction of soluble particles containing Na (soluble-Na) at depths from 0.01 m to 3.85 m. A significant amount of particles containing Cl, S, and soluble-Na are confirmed to exist in the surface snow. About half of the particles contain S and/or Na in any form, and about 20% of the particles contain Cl. Among all the particles containing Na, 76% are soluble.

[30] Table 1 shows the correlation coefficients between Cl, S, total-Na, and soluble-Na. The correlation coefficients in the top panel include all depths (0 to 4.0 m), while the lower set is based on all depths except for the prior year (0.1 to 4.0 m). At present, the annual accumulation of snow at the DF station is about 0.1 m (equivalent to 27.3 mm of water precipitation, as reported by *Kameda et al.* [2008]). There is no correlation between Cl and either type of Na (total nor soluble), probably due to nearly complete sea salt sulfatized. The correlation between S and soluble-Na is stronger than the correlation between S and total-Na. Also, the correlation between soluble-Na and S is stronger in a sample that excludes the prior year ($r^2 = 0.80$) than it is over the complete range of depths ($r^2 = 0.64$). These results strongly suggest that a large proportion of soluble-Na has combined with S as sodium sulfate, especially in snow deposited more than one year ago.

[31] Figure 3 shows the depth profiles of two mass ratios: S to soluble-Na and Cl to soluble-Na. The related ion concentration ratios SO_4^{2-} to Na^+ and Cl^- to Na^+ (weight/weight) are also shown in Figure 3 (data from *Hoshina* [2010]). The mass and ion ratios for Na and S exhibit similar fluctuations with depth, and the ion ratios are two to three times larger than the mass ratios. This similarity between the ion concentration depth profiles suggests that almost all Na^+ combines with SO_4^{2-} as sodium sulfate. Indeed, the consistency between the two mass ratios can be attributed entirely to the creation of sodium sulfate [*Iizuka et al.*, 2006]. The excess observed in the ion concentration ratios compared to the mass ratios is probably due to sulfuric acid [*Iizuka et al.*, 2006] in the sample, which does not appear as particles on the membrane filter. It has been suggested that the sulfuric acid exists at triple junctions and/or along grain boundaries in the ice core [*Mulvaney et al.*, 1988].

[32] The correlation between the mass and ion ratios is stronger in samples excluding the prior year ($r^2 = 0.74$; 0.1 m to 4.0 m) than over the entire range of depths ($r^2 = 0.38$). Again, this difference suggests that almost all soluble-Na has combined with S as sodium sulfate in snow deposited more than one year ago.

[33] Dealing now with the mass and ion concentration ratios of Cl and Na, we find that the mass ratios are about an order of magnitude smaller than the ion ratios at most
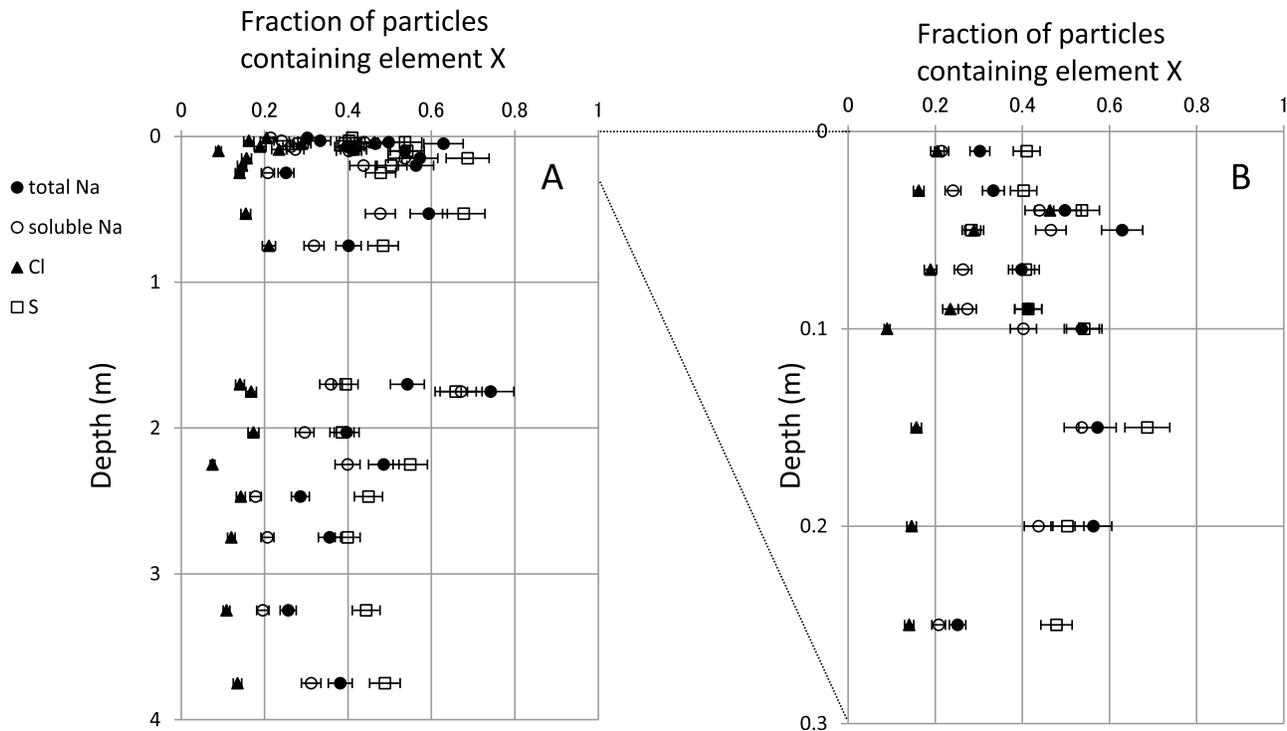
Figure 2. (a) Depth profiles for the proportion of particles containing Cl, S, Na, and soluble Na. (b) A close-up of the shallower part of Figure 2a. More than 99% of Cl and S in particles are soluble materials.

depths. This difference suggests that a certain amount of Cl^- exists as hydrochloric acid rather than sodium chloride [*Iizuka et al.*, 2006]. Note that hydrochloric acid will not appear as particles on the membrane filter. We found no correlation between the mass and ion ratios: $r^2 = 0.48$ in 0.1 to 4.0 m snow, and $r^2 = -0.10$ in 0 to 4.0 m snow.

4.2. Quantifying the Amount of Sea Salt Sulfatization in the Atmosphere

[34] This section estimates the moles of sodium chloride (M_{NaCl}) and sodium sulfate (M_{Na2SO4}) in the first 4.0 m of surface snow at Dome Fuji. In the above discussions, we showed evidence that 1) particles containing S and Cl are sulfate and chloride respectively; and 2) when Na coexists with S or Cl, that particle is soluble. We therefore assume that particles containing both Na and S consist of sodium sulfate, while those containing both Na and Cl consist of sodium chloride. The same assumptions are used by many studies analyzing present-day atmospheric aerosols by SEM-EDS [e.g., *Campos-Ramos et al.*, 2010]. Because melted DF snow samples contain mainly sodium, chloride, and sulfate ions [*Watanabe et al.*, 2003], we regard these assumptions as highly reliable.

[35] To determine the moles of sodium chloride, we compare M_{Na} to M_{Cl} for each particle. The moles (M_i; $i =$ Na, Cl, and S) are calculated from the total mass of each element, which in turn is inferred from the atomicity ratios observed by XDS (section 3). If $M_{Na} < M_{Cl}$, then M_{NaCl} (mol) is expressed as $M_{NaCl} = M_{Na}$. If $M_{Na} > M_{Cl}$, then M_{NaCl} (mol) is given by $M_{NaCl} = M_{Cl}$. In the case of sodium sulfate, if $M_{Na} < 2M_S$ then M_{Na2SO4} (mol) is expressed as $M_{Na2SO4} = 1/2\ M_{Na}$. If $M_{Na} > 2M_S$, then M_{Na2SO4} (mol) is given by $M_{Na2SO4} = M_S$.

[36] Figure 4 shows the molar ratio of M_{NaCl} to M_{Na2SO4} as a function of depth. On average, this ratio is higher within 0.1 m of the surface than in deeper snow. However, in the first 0.1 m of snow we also observe some very low molar ratios (less than 0.05), suggesting that almost all sodium chloride changed rapidly to sodium sulfate, either in the air or soon after it precipitated. The low ratios plausibly come from a summer with relatively high sulfuric acid content, and can be taken as evidence that sea salt sulfatization occurred mainly in the atmosphere for these layers. Likewise, the high ratios (greater than 0.1) in the first 0.1 m of snow may come from a winter layer with low sulfuric acid content and high sea salt content. Under these conditions, some sodium chloride could survive sulfatization in the atmosphere.

[37] When reconstructing past aerosols from the deep ice cores of inland Antarctica, we usually discuss fluctuations

Table 1. Correlation Coefficients Between the Proportions of Particles Containing Cl, S, Total Na, and Soluble Na, as Shown in Figure 2

|	Total Na	S	Cl	Soluble Na
		0–4.0 m		
Total Na	1			
S	0.46	1		
Cl	0.16	−0.14	1	
Soluble Na	0.95	0.64	0.19	1
		0.1–4.0 m		
Total Na	1			
S	0.68	1		
Cl	0.23	0.13	1	
Soluble Na	0.96	0.81	0.25	1
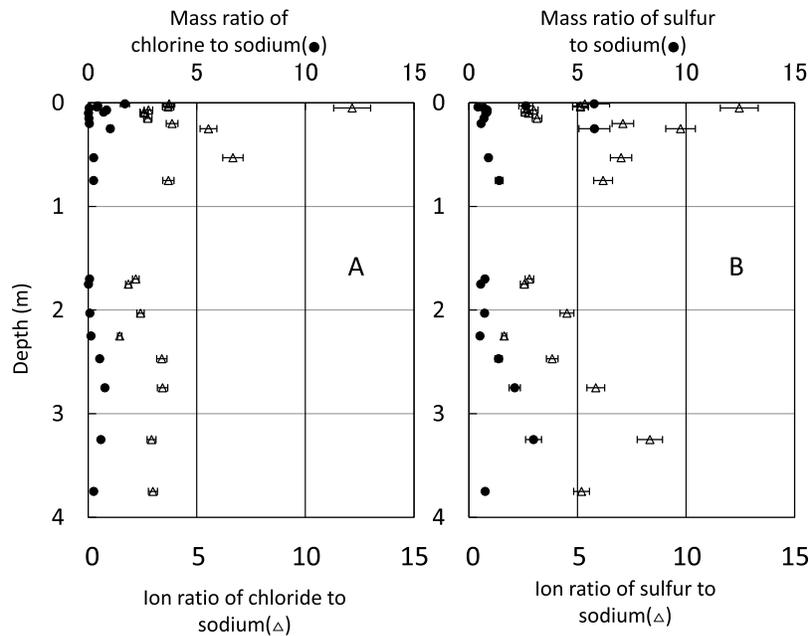
Figure 3. (a) The mass ratios of chlorine to soluble sodium are marked as black circles, estimated from the volumes of particles identified by EDS. The open triangles are ion concentration ratios of chloride to sodium, measured by IC. (b) The black circles are the mass ratios of sulfur to soluble sodium, and the open triangles are the ratios of sulfate ion to sodium ion concentrations.

on time scales of more than a decade (or at least one year). For this reason, from now on we base our calculations on two average values: the molar ratio in fresh (first year) snow is 0.18 (one-sigma confidence range 0.16∼0.20), and the molar ratio over the last decade of snow is 0.09 (0.08∼0.10). As a reference, 140 particles containing both Na and S, and 115 particles containing both Na and Cl, were used to calculate the first year's ratio of 0.18. A total of 921 and 288 particles containing (Na,S) and (Na,Cl) respectively were

used to calculate the ratio of 0.09. These ratios can be used to estimate the proportion of sea salt that sulfatized in the atmosphere, as we will describe below.

[38] According to the literature, there are two principal sources of sea salt in the snow: spray from the open sea [*Legrand et al.*, 1988] and frost flowers on sea ice [*Wolff et al.*, 2003]. *Rankin and Wolff* [2002] measured the mass ratio of SO_4^{2-} to Na^+ at a coastal site of Antarctica, obtaining average values of 0.25 and 0.1 for open
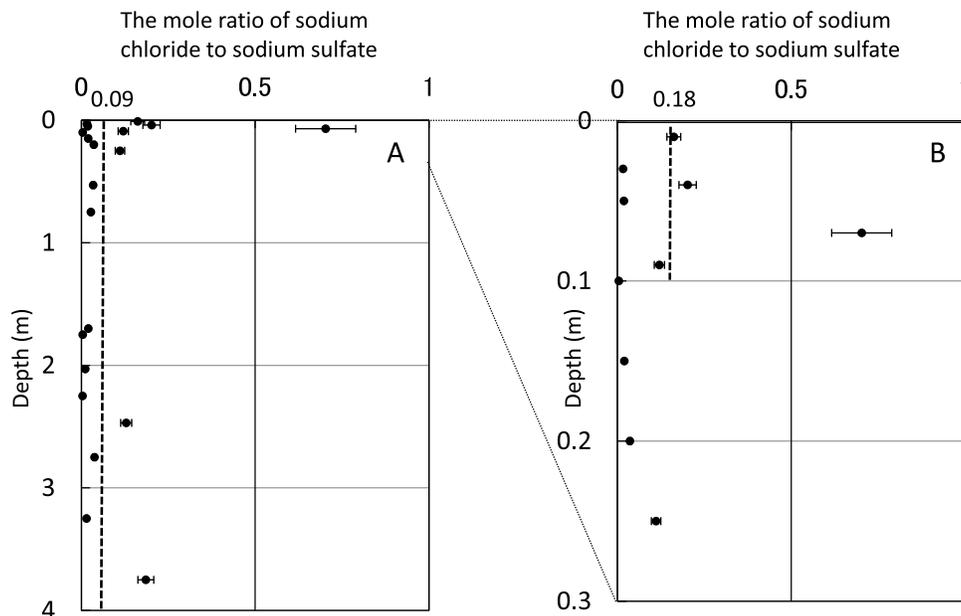
Figure 4. (a) Depth profile of the molar ratio of sodium chloride to sodium sulfate. (b) A close-up of the shallower part of Figure 4a.
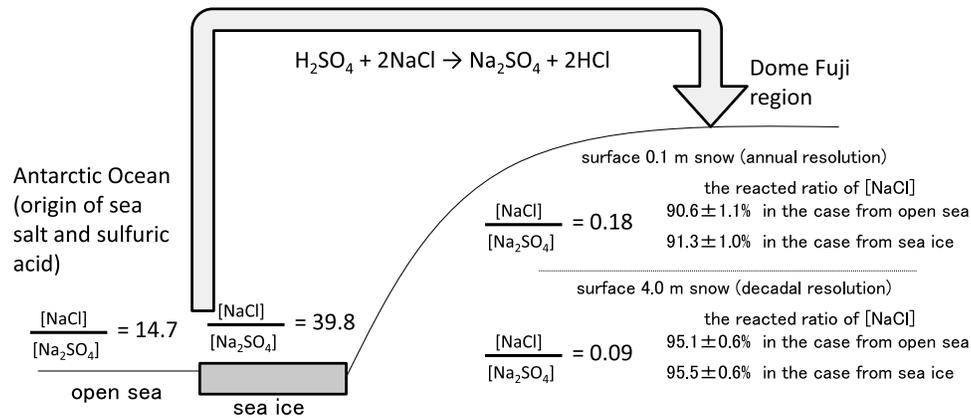
Figure 5. A schematic of sea salt sulfatization processes from the Antarctic Ocean to the surface snow of Dome Fuji.

seawater and sea ice respectively. These mass ratios can be transformed to molar ratios of 5.98×10^{-2} and 2.39×10^{-2} respectively. If we assume that all the SO_4^{2-} ions in sea salt react with Na^+, and that the remaining Na^+ ions compound with Cl^-, then the moles $[Na_2SO_4]$ and $[NaCl]$ can be calculated as shown below. This assumption leads to a lower limit on the ratio of M_{NaCl} to M_{Na2SO4} in the two sources.

$$[Na_2SO_4] = \left[SO_4^{2-}\right]$$

$$[NaCl] = [Na^+] - 2\left[SO_4^{2-}\right]$$

Thus, the molar ratio of $[NaCl]$ to $[Na_2SO_4]$ can be expressed as

$$\frac{[NaCl]}{[Na_2SO_4]} = \frac{[Na^+] - 2\left[SO_4^{2-}\right]}{\left[SO_4^{2-}\right]} = \frac{[Na^+]}{\left[SO_4^{2-}\right]} - 2$$

Substituting in Rankin's values, we find that the molar ratios of NaCl to Na_2SO_4 are 14.7 and 39.8 in open seawater and sea ice respectively (Figure 5).

[39] As shown in Figures 4 and 5, the annual and decadal average molar ratios in the snow are 0.18 (0.16~0.20) and 0.09 (0.08~0.10) respectively. If the salt originated in sea ice, the molar ratio would have had to decrease from 39.8 to 0.18 (0.16~0.20) over the course of a year, as the salt was transported through the atmosphere from the Antarctic Ocean to inland Antarctica. Over a decade, the molar ratio had to decrease from 0.18 to 0.09 (0.08~0.10) from post-depositional effects.

[40] If we denote $[Na_2SO_4]$ at the source as k (>0) (mol), then $[NaCl]$ at the source is $39.8k$ (mol). If the rate of $[Na_2SO_4]$ production is n (mol), then the amount of $[NaCl]$ that must react is $2n$ (mol). This notation leads to the following expression:

$$\frac{[NaCl]}{[Na_2SO_4]} = \frac{39.8k - 2n}{k + n} = 0.18(0.16 \sim 0.20)$$

Solving this equation yields $n = 18.2k$ (18.0k~18.4k) (mol). $[NaCl]$ in the surface snow can be expressed as $3.45k$ (3.06k~3.84k). The amounts of $[NaCl]$ present at the source and in the first year of snow are $39.8k$ and $3.45k$ (3.06k~3.84k) respectively. Thus, about 91.3% (90.4%~92.3%) of the initial sea salt (sodium chloride) is removed by sulfatization in the atmosphere and in the uppermost layer of snow within one year after precipitation (Figure 5).

[41] In the same way, substituting 0.09 (0.08~0.10) for 0.18 (0.16~0.20) in the above relation tells us that about 95.5% (94.9%~96.0%) of the initial sea salt (sodium chloride) is removed by sulfatization in the atmosphere and by post-depositional processes in the surface snow over ten years (Figure 5).

[42] The results just derived assume that the salt originated from sea ice. If the salt instead originated from the open sea, we can repeat the calculations with a different initial molar ratio. Without entering into the details, $[NaCl]$ at the source should be $14.7k$ (mol). The $[NaCl]$ values at the source, in the first 0.1 m of surface snow, and in the deeper snow are $14.7k$, $1.38k$ (1.22k~1.53k), and $0.72k$ (0.63k~0.80k) respectively. In this scenario, about 90.6% (89.6%~91.7%) of the initial sea salt is removed by sulfatization in the first year, and 95.1% (94.5%~94.7%) is removed after ten years (Figure 5).

[43] As described in the Introduction, the main seasonal difference in ion concentrations is that in the summer, SO_4^{2-} concentrations are maximized in the atmosphere and minimized in fresh snow. If we focus on fresh snow [*Iizuka et al.*, 2004, Figure 1], we find that the seasonal trends of Na^+ and SO_4^{2-} are synchronized, with the SO_4^{2-} concentration being similar to or slightly higher than the Na^+ concentration in mole equivalent. This suggests that throughout the year, even during the summer when sulfuric acid is high and sea salt is low, the SO_4^{2-} concentration in fresh snow is controlled by the Na^+ concentration. We propose that the seasonal difference between the two trends can be explained by the process of aerosols being deposited from atmosphere to snow ("fallout"), and by the differences between Na_2SO_4 in solid form and H_2SO_4 (SO_2 gas in the atmosphere). Solid Na_2SO_4, formed by the reaction $H_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2HCl$ in atmosphere, is likely to be deposited on snow. SO_2 gas, on the other hand, is not likely to be deposited on fresh snow as H_2SO_4, but remain a gaseous phase in atmosphere. Thus, although a

Table A1. Sample Depth, Average Size of Nonvolatile Particles, and Average Size of Insoluble Particles in Three Ice Samples[a]

	Nonvolatile Particles (μm)	Insoluble Particles (μm)
0.07 m section	3.23 ± 1.60	3.41 ± 1.51
3.25 m section	3.22 ± 1.36	3.19 ± 1.38
18.0 m section	2.65 ± 1.41	2.86 ± 1.48

[a]The uncertainties are one standard deviation, and each sample yielded at least 180 insoluble particles.

certain amount of sulfate can be supplied by H_2SO_4, the majority of SO_4^{2-} is precipitated in the form of solid Na_2SO_4.

[44] We cannot completely distinguish between the processes of sulfatization occurring in the atmosphere or in the snow layer within one year after particle deposition. However, redistribution processes from some studies [e.g., *Wagnon et al.*, 1999] point out that chloride decreases with depth over the first several meters of snowpack in Dome C and Vostok. If these processes require several decades (several meters of snowpack) to occur, then the rate of sulfatization in the snow layer is also likely to be very slow in the first year after being deposited, which corresponds to several centimeters of snowpack. We therefore conclude that the observed evolution in molar ratios is primarily due to sulfatization that occurred in the atmosphere.

[45] If a certain amount of reaction between nitrate acid and sea salt also occurred in the Antarctic atmosphere, then we should consider the molar ratio NaCl / (NaNO$_3$ + Na$_2$SO$_4$) rather than NaCl / Na$_2$SO$_4$. However, NaCl / (NaNO$_3$ + Na$_2$SO$_4$) has a lower value than NaCl / Na$_2$SO$_4$, so ignoring the contribution of nitrate acid would lead us to underestimate the proportion of sea salt that underwent sulfate reactions in the atmosphere or the uppermost snow layer. Thus, even if we consider the effect of the nitrate reaction, our main conclusion does not change.

[46] At annual resolution, our analysis clearly suggests that about 90% of the sea salt underwent sulfatization during its fallout over Dome Fuji or in the snow layer within one year after being deposited. Among the several glacial and interglacial periods recorded by the DF core, the present climate (Holocene) is one of the most acidic [e.g., *Iizuka et al.*, 2008]. One way to explain this high acidity of the Holocene is that, during colder periods than the present environment, a higher flux of sea salt and soluble continental minerals (e.g., CaCO$_3$) probably entered the atmosphere, in a manner similar to that described here for modern sea salt [e.g., *Iizuka et al.*, 2008]. The greater availability of reactants would have more rapidly depleted the sulfuric acid, so we would expect an even higher sulfatization ratio compared to the present. These findings also imply that aerosol sulfatization in past cycles was more likely to occur in the atmosphere or fallout stages, rather than after being deposited.

[47] In summary, the fact that sulfatization is close to completion in freshly fallen snow implies that little or no additional sulfatization of sea salt takes place in the deep ice cores. We therefore claim that the aerosol compounds discovered in Dome Fuji ice cores accurately reflect the atmospheric chemistry's effects on sea salts and continental minerals at the time the snow layer was formed.

5. Conclusion

[48] Using SEM-EDS technology, we measured the constituent elements of nonvolatile particles in samples of surface snow to a depth of 4 m at the Dome Fuji station with a decadal time-resolution, which is same resolution of ion fluxes analyzed from Dome Fuji ice core. Soluble particles containing Na with either Cl or S are confirmed to exist in the surface snow. About half of the particles contain S or Na, and about 20% contain Cl. Among all Na-containing particles, 76% are soluble. We observe that Cl ratios are higher within 0.1 m of the surface than in snow taken from depths between 0.1 and 4.0 m.

[49] We measured the mass ratio of sulfur to soluble sodium, and the ion concentration ratio of SO_4^{2-} to Na^+. The two ratios vary with depth in a similar pattern, and in deep snow their trends are closely synchronized, suggesting that almost all Na^+ are combined with SO_4^{2-} as sodium sulfate. On the other hand, when comparing the mass ratio of Cl to
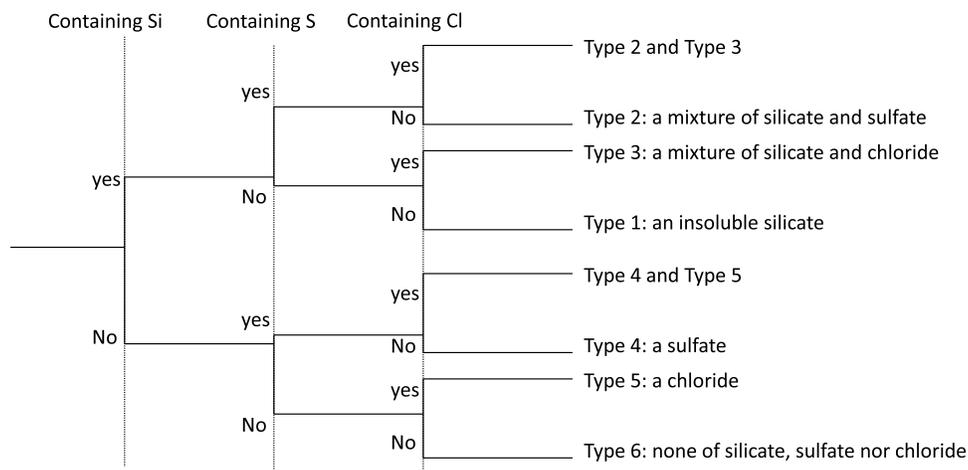
Figure A1. Classification scheme dividing the particles into six types based on their measured constituents. These types are identified using our method for dividing soluble and insoluble particles [*Iizuka et al.*, 2009].
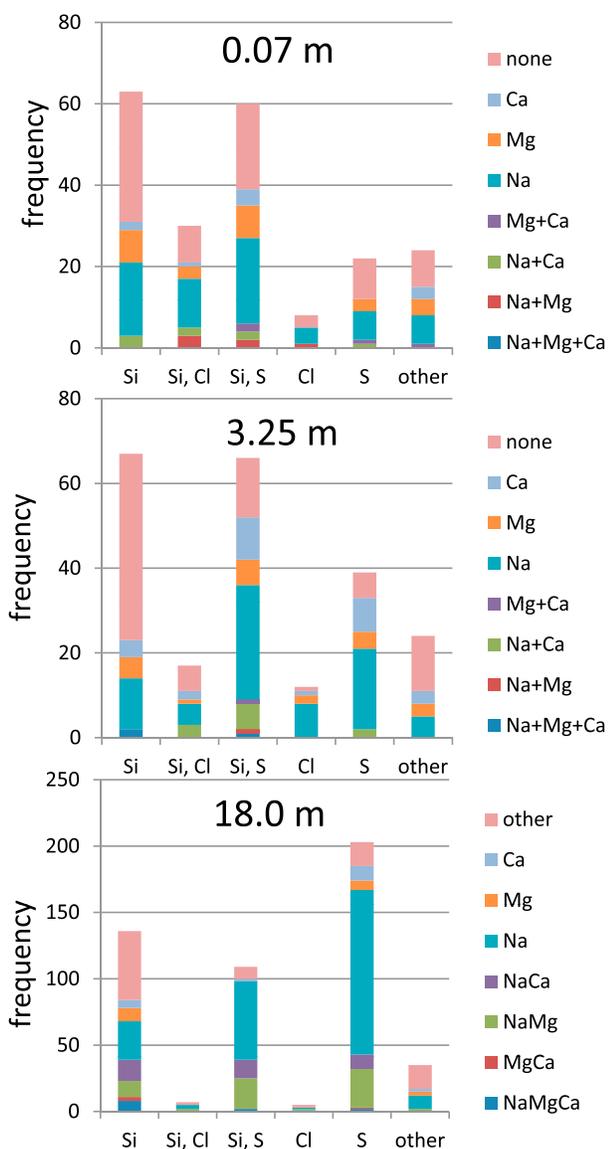
Figure A2. Frequencies of various elemental compositions in nonvolatile particles (those remaining after sublimation) from the 0.07, 3.75, and 18.0 m snow sections. The constituent elements are described in Figure A1.

soluble-Na with the ion ratio of Cl$^-$ to Na$^+$, the former is about an order of magnitude smaller. This difference suggests that a certain amount of Cl$^-$ exists as hydrochloric acid rather than sodium chloride.

[50] We then estimated the molar ratio of sodium chloride (M_{NaCl}) to sodium sulfate (M_{Na2SO4}), and calculated the amount of sea salt that would have had to sulfatize in the atmosphere during transport, as compared to the amount that sulfatized during fallout and in the fresh surface snow. The molar ratio in the first year's snow (0.18 on average) is extremely low compared to that of salt originating in open sea or sea ice (14.7 or 39.8), respectively. We estimate that on average, about 90% of the initial sea salt sulfatized in the first year. When taking into account the seasonal trends of

ion species in the fresh snow [*Iizuka et al.*, 2004, Figure 1], we can conclude that almost all of the SO$_4^{2-}$ precipitated in the form of sodium sulfate. This fallout process was probably the major contributor to the 90% of sea salt that sulfatized in the first year.

Appendix A: How to Divide Nonvolatile Particles Into Insoluble and Soluble Particles

[51] For three randomly selected samples taken from depths of 0.07, 3.25, and 18 m, we immersed the filter in ultra-pure water at 25°C for about 50 h after the SEM-EDS measurement, which is enough time to dissolve all soluble constituents. The insoluble particles remaining on the filter were then analyzed again using SEM-EDS. In this way, we obtained separate measurements of nonvolatile and insoluble particles from the same sample.

[52] Table A1 lists the average diameters and standard deviations of nonvolatile particles (those remaining after sublimation) and insoluble particles (those remaining after immersing the nonvolatile particles in water for 50 h) in each ice sample. We cannot detect a significant relationship between particle diameter and elemental composition. Hence, in some of the discussions to follow, we assume that the number of particles identified as a given element is directly proportional to the volume of material composed of that element. An important motivation for adopting this simplified method is to allow researchers without access to SEM-EDS equipment to validate the results. We are not sure why particle diameters should be similar between insoluble and nonvolatile particles; however, a simple explanation would be that the process of transportation from the sea to DF is not efficient for particles larger and heavier than several μm [e.g., *Fattori et al.*, 2005].

[53] We focus on the six elements Si, S, Cl, Na, Mg, and Ca due to their strong associations with dust and ion concentrations. Nearly all the particles contained at least one of these elements. We have provided a distribution diagram (Figure A1) of the various types defined below.

1. Type 1: Si was detected but not S or Cl, implying a kind of silicate.

2. Type 2: Si and S were detected, implying a mixture of silicate and sulfate.

3. Type 3: Si and Cl were detected, implying a mixture of silicate and chloride.

4. Type 4: S was detected but not Si, implying a kind of sulfate.

5. Type 5: Cl was detected but not Si, implying a kind of chloride.

6. Type 6: No Si, S or Cl was detected.

[54] Within each type, we also classified particles according to their cationic combination (i.e., whether they contained Na, Mg, and/or Ca).

[55] Figures A2 and A3 show the frequency distribution of nonvolatile and insoluble particle types found in each ice section. Among the insoluble particles, 94.6% and 4.3% were Type 1 or Type 6 respectively (Figure A3). In contrast, among nonvolatile particles (Figure A2), from 42.7% to 65.5% contain sulfur or chlorine (Types 2 through 4). Thus, almost all sulfates and chloride are dissolved and ionized in the melting process, which changes Type 2 and Type 3
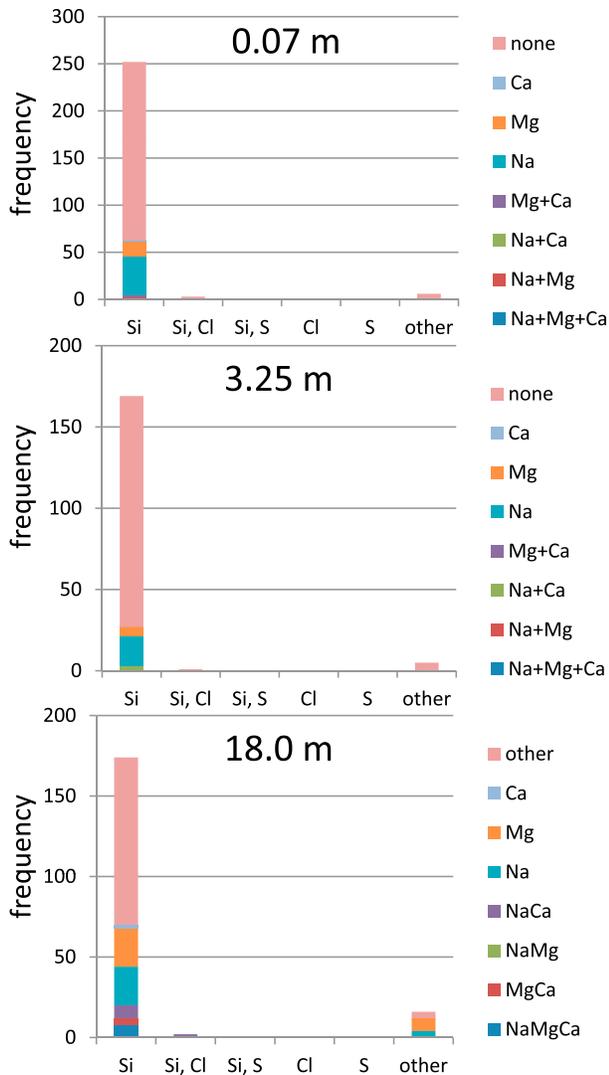
Figure A3. As Figure A2, but for insoluble particles (those remaining after immersing the nonvolatiles in water for 50 h).

particles into Type 1 particles. The distributions shown in Figure A3 suggest that insoluble particles contain mainly silicate minerals [e.g., *De Angelis et al.*, 1984], while soluble particles contain mainly sulfate and chloride salts. Based on Figure A3, Table A2 shows the proportion of insoluble particles containing calcium or sodium in each of the three sections. These elements, both insoluble and soluble particles, are primary components of aerosols in the Dome Fuji

ice core [*Watanabe et al.*, 2003], so play an important role in paleo-environment reconstruction from the DF ice core.

[56] According to Figure A2, the most common combination in soluble particles is Na and S (light blue in types 3 and 5). This result indicates the existence of sodium sulfate at all depths in the Dome Fuji snow. In the 0.07 m section, the combination of Na and Cl is also very important (light blue in types 2 and 4), indicating the existence of sodium chloride in surface snow. The reason for the differences in particle types at the three depths is described in the main text (see section 4.1).

[57] Figure A2 visualizes the proportion of insoluble particles containing calcium or sodium in each of the three sections (Table A2). For the sake of comparison, following a method that we developed in previous work dealing with Last Glacial Maximum ice [*Iizuka et al.*, 2009], we can also infer this ratio from our measurements of nonvolatile particles by making the following assumptions: (1) any calcium (sodium) in a Type 1 (silicate) particle is insoluble; (2) any calcium (sodium) in a particle of Type 2, 3, 4,or 5 is soluble; (3) Type 2 and Type 3 particles with calcium (sodium) change to Type 1 particles without calcium (sodium) when immersed in water; and (4) all Type 1 particles are insoluble. Thus, among nonvolatiles, the only insoluble particles containing calcium or sodium are of Type 1. However, Types 1, 2 and 3 are all considered insoluble.

[58] The *inferred* ratio of insoluble particles containing calcium to all insoluble particles is therefore

$$N_{type1\_Ca}/\left(N_{type1} + N_{type2} + N_{type3}\right).$$

The corresponding ratio for insoluble particles containing sodium is

$$N_{type1\_Na}/\left(N_{type1} + N_{type2} + N_{type3}\right).$$

N_{type1_Ca} and N_{type1_Na} are the numbers of Type 1 particles containing calcium and sodium respectively. For both calcium and sodium, the measured and inferred ratios are very similar, differing by at most three percentage points (Table A2). The consistency of these results strongly suggests that we have correctly interpreted the roles of calcium and sodium in each type of particle.

[59] Although the inference method just described was developed for an analysis of LGM ice [*Iizuka et al.*, 2009], this agreement implies that it is equally valid during one of the warmest climate periods (Holocene). The Holocene and glacial maximum periods are taken from opposite ends of the ice core [e.g., *Iizuka et al.*, 2008]. At depths where the ice temperature is above the eutectic temperature of one of these salts, however, this issue of particle types should be considered more cautiously.

Table A2. The Four Columns Report the Proportions of Insoluble Particles Containing Ca and the Proportions of Insoluble Particles Containing Na[a]

	Insoluble Ca / Insoluble Total From the Insoluble Particles	Insoluble Ca / Insoluble Total From the Nonvolatile Particles	Insoluble Na / Insoluble Total From the Insoluble Particles	Insoluble Na / Insoluble Total From the Nonvolatile Particles
0.07 m section	0.02 (±<0.005)	0.02 (±<0.005)	0.17 ± 0.01	0.19 ± 0.02
3.25 m section	0.02 (±<0.005)	0.04 ± 0.01	0.14 ± 0.01	0.11 ± 0.02
18.0 m section	0.13 ± 0.01	0.13 ± 0.01	0.23 ± 0.02	0.26 ± 0.02

[a]Each ratio is calculated in two ways; see Appendix A for details.

References

Andreae, M. O. (1995), Climatic effects of changing atmospheric aerosol levels, in *Future Climates of the World: A Modeling Perspective*, *World Surv. Climatol.*, vol. 16, edited by A. Henderson-Sellers, pp. 347–398, Elsevier, Amsterdam, doi:10.1016/S0168-6321(06)80033-7.

Campos-Ramos, A., A. A. Piña, X. Querol, and A. Alastuey (2010), Methodology for the characterization and identification by sem-eds of atmospheric particles from different pollutions emission, in *Microscopy: Science, Technology, Applications and Education*, vol. 1, edited by A. Mendez-Vilas and J. Diaz, pp. 329–333, Formatex Res. Cent, Badajoz, Spain.

De Angelis, M., M. Legrand, J. R. Petit, N. I. Barkov, Y. S. Korotkevitch, and V. M. Kotlyakov (1984), Soluble and insoluble impurities along the 950 m Deep Vostok Ice Core (Antarctica)—Climatic implications, *J. Atmos. Chem.*, 1, 215–239, doi:10.1007/BF00058730.

Delmas, R. J., M. De Angelis, Y. Fujii, K. Goto-Azuma, K. Kamiyama, J. R. Petit, and O. Watanabe (2003), Linking Antarctic glaciochemical records to past climate conditions, *Mem. Natl Inst. Polar Res., Spec. Issue*, 57, 105–120.

EPICA Community Members (2004), Eight glacial cycles from an Antarctic ice core, *Nature*, 429, 623–628, doi:10.1038/nature02599.

EPICA Community Members (2006), One-to-one coupling of glacial climate variability in Greenland and Antarctica, *Nature*, 444, 195–198, doi:10.1038/nature05301.

Fattori, I., S. Becagli, S. Bellandi, E. Castellano, M. Innocenti, A. Mannini, M. Severi, V. Vitale, and R. Udisti (2005), Chemical composition and physical features of summer aerosol at Terra Nova Bay and Dome C, Antarctica, *J. Environ. Monit.*, 7, 1265–1274, doi:10.1039/b507327h.

Hara, K., K. Osada, M. Kido, M. Hayashi, K. Matsunaga, Y. Iwasaka, T. Yamanouchi, G. Hashida, and T. Fukatsu (2004), Chemistry of sea-salt particles and inorganic halogen species in Antarctic regions: Compositional differences between coastal and inland stations, *J. Geophys. Res.*, 109, D20208, doi:10.1029/2004JD004713.

Hoshina, Y. (2010), Postdepositional changes in water stable isotopes in snowpack at Dome Fuji, Antarctica [in Japanese], MS thesis, Nagoya Univ., Nagoya, Japan.

Igarashi, M., et al. (2011), Dating of the Dome Fuji shallow ice core based on a record of volcanic eruptions from AD 1260 to AD 2001, *Polar Sci.*, 5, 411–420, doi:10.1016/j.polar.2011.08.001.

Iizuka, Y., Y. Fujii, N. Hirasawa, T. Suzuki, H. Motoyama, T. Furukawa, and T. Hondoh (2004), SO_4^{2-} minimum in summer snow layer at Dome Fuji, Antarctica and the probable mechanism, *J. Geophys. Res.*, 109, D04307, doi:10.1029/2003JD004138.

Iizuka, Y., T. Hondoh, and Y. Fujii (2006), Na_2SO_4 and $MgSO_4$ salts during Holocene period in a Dome Fuji ice core derived by high depth-resolution analysis, *J. Glaciol.*, 52, 58–64, doi:10.3189/172756506781828926.

Iizuka, Y., et al. (2008), A relationship between ion balance and the chemical compounds of salt inclusions found in the GRIP and Dome Fuji ice cores, *J. Geophys. Res.*, 113, D07303, doi:10.1029/2007JD009018.

Iizuka, Y., T. Miyake, M. Hirabayashi, T. Suzuki, S. Matoba, H. Motoyama, Y. Fujii, and T. Hondoh (2009), Constituent elements of insoluble and nonvolatile particles during the Last Glacial Maximum of the Dome Fuji ice core, *J. Glaciol.*, 55(191), 552–562, doi:10.3189/002214309788816696.

Johnsen, S. J., W. Dansgaard, H. B. Clausen, and C. C. Langway Jr. (1972), Oxygen isotope profiles through the Antarctic and Greenland ice sheets, *Nature*, 235(5339), 429–434, doi:10.1038/235429a0.

Jourdain, B., S. Preunkert, O. Cerri, H. Castebrunet, R. Udisti, and M. Legrand (2008), Year round record of size segregated aerosol composition in central Antarctica (Concordia station): Implications for the degree of fractionation of sea salt particles, *J. Geophys. Res.*, 113, D14308, doi:10.1029/2007JD009584.

Kameda, T., H. Motoyama, S. Fujita, and S. Takahashi (2008), Temporal and spatial variability of surface mass balance at Dome Fuji, East Antarctica, by the stake method from 1995 to 2006, *J. Glaciol.*, 54(184), 107–116, doi:10.3189/002214308784409062.

Legrand, M. R., C. Lorius, N. I. Barkov, and V. N. Petrov (1988), Vostok (Antarctica) ice core: Atmospheric chemistry changes over the last climatic cycle (160,000 years), *Atmos. Environ.*, 22(2), 317–331, doi:10.1016/0004-6981(88)90037-6.

Mulvaney, R., and E. W. Wolff (1994), Spatial variability of the major chemistry of the Antarctic ice sheet, *Ann. Glaciol.*, 20, 440–447, doi:10.3189/172756494794587159.

Mulvaney, R., E. W. Wolff, and K. Oates (1988), Sulphuric acid at grain boundaries in Antarctic ice, *Nature*, 331, 247–249, doi:10.1038/331247a0.

Ohno, H., M. Igarashi, and T. Hondoh (2005), Salt inclusions in polar ice core, Location and chemical form of water-soluble impurities, *Earth Planet. Sci. Lett.*, 232(1–2), 171–178, doi:10.1016/j.epsl.2005.01.001.

Petit, J. R., et al. (1999), Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, 399, 429–436, doi:10.1038/20859.

Rankin, A. M., and E. W. Wolff (2002), Frost flowers: Implications for tropospheric chemistry and ice core interpretation, *J. Geophys. Res.*, 107(D23), 4683, doi:10.1029/2002JD002492.

Röthlisberger, R., R. Mulvaney, E. W. Wolff, M. A. Hutterli, M. Bigler, M. De Angelis, M. E. Hansson, J. P. Steffensen, and R. Udisti (2003), Limited dechlorination of sea salt aerosols during the last glacial period: Evidence from the EPICA Dome C ice core, *J. Geophys. Res.*, 108(D16), 4526, doi:10.1029/2003JD003604.

Udisti, R., S. Becagli, S. Benassai, M. De Angelis, M. E. Hansson, J. Jouzel, J. Schwander, J. P. Steffensen, R. Traversi, and E. Wolff (2004), Sensitivity of chemical species to climate changes in the 45 kyr as revealed by high-resolution Dome C (East Antarctica) deep ice core, *Ann. Glaciol.*, 39, 457–466, doi:10.3189/172756404781814096.

Wagnon, P., R. J. Delmas, and M. Legrand (1999), Loss of volatile acid species from upper firn layers at Vostok, Antarctica, *J. Geophys. Res.*, 104, 3423–3431, doi:10.1029/98JD02855.

Watanabe, O., J. Jouzel, S. Johnsen, F. Parrenin, H. Shoji, and N. Yoshida (2003), Homogeneous climate variability across East Antarctica over the past three glacial cycles, *Nature*, 422(6931), 509–512, doi:10.1038/nature01525.

Wolff, E. W., A. M. Rankin, and R. Rothlisberger (2003), An ice core indicator of Antarctic sea ice production?, *Geophys. Res. Lett.*, 30(22), 2158, doi:10.1029/2003GL018454.

K. Fujita and Y. Hoshina, Graduate School of Environmental Studies, Nagoya University, Nagoya 464-8601, Japan.

S. Fujita, H. Motoyama, and F. Nakazawa, National Institute of Polar Research, Tokyo 190-8518, Japan.

M. Hansson and T. Karlin, Department of Physical Geography and Quaternary Geology, Stockholm University, SE-106 91 Stockholm, Sweden.

Y. Iizuka, T. Sakurai, and A. Tsuchimoto, Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan. (iizuka@lowtem.hokudai.ac.jp)