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<td>Author(s)</td>
<td>Oyabu, Ikumi; Iizuka, Yoshinori; Uemura, Ryu; Miyake, Takayuki; Hirabayashi, Motohiro; Motoyama, Hideaki; Sakurai, Toshimitsu; Suzuki, Toshitaka; Honda, Takeo</td>
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<tr>
<td>Citation</td>
<td>Journal of geophysical research : atmospheres, 119(24): 14045-14058</td>
</tr>
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<td>Issue Date</td>
<td>2014-12-27</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/59422">http://hdl.handle.net/2115/59422</a></td>
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<tr>
<td>Rights</td>
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<td>Type</td>
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<tr>
<td>File Information</td>
<td>jgrd51827.pdf</td>
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<td>Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP</td>
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Chemical compositions of sulfate and chloride salts over the last termination reconstructed from the Dome Fuji ice core, inland Antarctica

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Abstract The flux and chemical composition of aerosols impact the climate. Antarctic ice cores preserve the record of past atmospheric aerosols, providing useful information about past atmospheric environments. However, few studies have directly measured the chemical composition of aerosol particles preserved in ice cores. Here we present the chemical compositions of sulfate and chloride salts from aerosol particles in the Dome Fuji ice core. The analysis method involves ice sublimation, and the period covers the last termination, 25.0–11.0 thousand years before present (kyr B.P.), with a 350 year resolution. The major components of the soluble particles are CaSO4, Na2SO4, and NaCl. The dominant sulfate salt changes at 16.8 kyr B.P. from CaSO4, a glacial type, to Na2SO4, an interglacial type. The sulfate salt flux (CaSO4 plus Na2SO4) inversely correlates with δ18O in Dome Fuji over millennial timescales. This correlation is consistent with the idea that sulfate salt aerosols contributed to the last deglacial warming of inland Antarctica by reducing the aerosol indirect effect. Between 16.3 and 11.0 kyr B.P., the presence of NaCl suggests that winter atmospheric aerosols are preserved. A high NaCl/Na2SO4 fraction between 12.3 and 11.0 kyr B.P. indicates that the contribution from the transport of winter atmospheric aerosols increased during this period.

1. Introduction

The concentrations of impurities in an Antarctic deep ice core can be used as climate proxies to reconstruct the history of aerosols over the past several hundred thousand years [e.g., Watanabe et al., 2003a; EPICA Community Members, 2004, 2006]. In Antarctic ice cores, insoluble aerosols mainly contain silicates, whereas soluble aerosols contain Na+, Mg2+, Ca2+, K+, NH4+, H+, SO42−, NO3−, Cl−, and methanesulfonic acid. Such proxies have revealed past climate variability on various timescales at high southern latitudes, including environmental changes in the southern parts of South America and the Southern Ocean [e.g., Fujii et al., 2003; Wolff et al., 2006, 2010; Kaiser and Lamy, 2010]. Primary aerosol particles are emitted directly from land and/or the sea surface, whereas secondary aerosols such as sulfate and nitrate compounds are produced by chemical reactions in the atmosphere. For example, CaSO4 can be a primary aerosol, generated by terrestrial gypsum (CaSO4 · 2H2O), and also a secondary aerosol, generated by neutralization of calcium carbonate (CaCO3) by H2SO4 in the atmosphere [Legrand et al., 1997]. Na2SO4, a secondary aerosol, mainly comes from oceanic NaCl reacting with H2SO4 in the atmosphere [Legrand and Delmas, 1988; Iizuka et al., 2012a]. Clarifying the abundance of such primary and secondary aerosols is important for understanding past atmospheric environments. Sulfate aerosols are a key component of cloud condensation nuclei (CCN) in the atmosphere [Intergovernmental Panel on Climate Change (IPCC), 2007, 2013]. According to Köhler theory [Köhler, 1936], a larger aerosol particle has a lower critical supersaturation for CCN activation, which makes it more likely to become CCN. Hygroscopicity will also affect CCN activation. However, in comparing H2SO4 to sulfate salt, the effect from the difference in hygroscopicity is negligibly small compared to the typical differences in particle size [Petters and Kreidenweis, 2007]. That is, the sulfate salt, being mainly secondary aerosols of dust and sea salt [Legrand et al., 1997; Legrand and Delmas, 1988], have diameters typically exceeding 1 μm, much larger than the submicron diameters of H2SO4 droplets [e.g., Whitby, 1978]. Moreover, Jasper et al. [2011] argued...
that \( H_2SO_4 \) is too small to be CCN, so other chemical species are needed for particle growth. Thus, CCNs are most likely more dominated by sulfate salts than by \( H_2SO_4 \).

Several studies have deduced the salt compositions from the measured ion concentrations [Legrand et al., 1988; Iizuka et al., 2008]. For Vostok ice, Legrand et al. [1988] calculated the sea-salt and terrestrial-salt concentrations by using seawater composition. They argued that the Holocene soluble impurities were mainly \( H_2SO_4 \), HNO₃, HCl, NaCl, and Na₂SO₄. For the Last Glacial Maximum (LGM), the ice instead contained primarily \( H_2SO_4 \), NaCl, and CaSO₄. For Dome Fuji ice, Iizuka et al. [2008] developed an ionic balance method for determining the chemical compounds of impurities. Following a suggestion by Röthlisberger et al. [2003a], a previous finding of Iizuka et al. [2006], and a result later published by Sakurai et al. [2011], they assumed that \( Ca^{2+} \) forms sulfate prior to Na⁺, Na⁺ forms Na₂SO₄ prior to NaCl, and Ca²⁺ forms sulfate prior to nitrate. For the LGM, they deduced that there were CaSO₄, Na₂SO₄, NaCl, and negligible \( H_2SO_4 \), whereas the Holocene had Na₂SO₄, \( H_2SO_4 \), little CaSO₄, and negligible NaCl.

Earlier studies used micro-Raman spectroscopy to measure micron-sized single particles in ice cores. In the Dome Fuji ice core, Ohno et al. [2005] found soluble impurities of \( CaSO_4 \cdot 2H_2O \), MgSO₄ · 11H₂O, and Na₂SO₄ · 10H₂O. Later, Ohno et al. [2006] showed that the primary soluble impurities are \( CaSO_4 \cdot 2H_2O \) for the glacial maxima and \( NaSO_4 \cdot 10H_2O \) and MgSO₄ · 11H₂O for warm periods. Using the same method, Sakurai et al. [2011] measured the Dome Fuji ice of the last termination and suggested that most of the \( Ca^{2+} \) exists as \( CaSO_4 \cdot 2H_2O \) and that the sulfate salt compositions from LGM to Holocene can be explained by ion balance arguments.

Iizuka et al. [2009] developed the sublimation-EDS (energy dispersive X-ray spectroscopy) method, which allows one to measure statistically significant numbers of chemical compositions of soluble and insoluble particles in an ice core sample. Using this method, Iizuka et al. [2012a, 2013] showed that sea salt in Talos Dome, a peripheral dome, remains a primary aerosol as NaCl during warm periods, whereas more than 90% of the sea salt in Dome Fuji came from a secondary aerosol as Na₂SO₄. With the same method, Iizuka et al. [2012b] presented a time series data set of soluble salts (\( CaSO_4 \), Na₂SO₄, and NaCl) and the mixture of dust and sulfates over the last 300 kyr. In contrast to the nearly constant \( SO_4^{2-} \) (\( CaSO_4 \), Na₂SO₄, and \( H_2SO_4 \)) flux (consistent with findings at Dome C [Wolff et al., 2010]), the sulfate salt (\( CaSO_4 \) and Na₂SO₄) flux inversely correlates with temperature. This correlation suggests that the glacial-to-interglacial decrease in sulfate salts reduces the aerosol indirect effect, a decrease that may contribute to the Antarctic warming.

The last glacial termination, approximately 25.0–11.0 kyr B.P., is an important period for which to investigate relations between temperature change and the chemical composition of aerosols. In this period, the chemical compositions of soluble aerosols changed drastically [Sakurai et al., 2011; Iizuka et al., 2012b] in conjunction with the climate, which showed a warming in the Dome Fuji region of approximately 8°C [Uemura et al., 2012]. The temperature starts increasing around 18 kyr B.P., stagnates during 16.0–14.7 kyr B.P., and then cools during 14.7–12.7 kyr B.P. at the Antarctic Cold Reversal (ACR) [Stenni et al., 2011]. After the ACR, the temperature rises again, reaching its highest value around 11 kyr B.P. The cause of this fluctuation has been explained by the bipolar seesaw [Stocker and Johnsen, 2003], in which the temperatures of the two hemispheres oscillate via a coupling involving the Atlantic Meridional Overturning Circulation and atmospheric circulation [Anderson et al., 2009; Barker et al., 2009]. Aerosols may supply clues about these temperature changes. However, the highest time resolution study of chemical compounds of soluble and insoluble particles in this period has only eight points [Sakurai et al., 2011], so the nature of the particles during the transition remains unclear. To clarify how the chemical compositions of these particles have changed, we analyzed the aerosol preserved in the Dome Fuji ice core with a higher time resolution.

2. Experimental Method

2.1. Ice Core Sample

The Dome Fuji ice core was drilled at one of the highest positions of the East Antarctic ice sheet (77.2°S, 39.4°E; 3810 m asl) from 1995 to 1997. The core is 2503 m long and covers the past 340 kyr [Watanabe et al., 2003a]. The ice core was stored in a cold room at −50°C, which is below the eutectic temperatures of all major salts. The sample depths used here are from 326.4 m (early Holocene: 11.0 kyr B.P.) to 579.8 m (LGM: 25.0 kyr B.P.). We selected 39 core sections, each section being a cuboid of 100 × 30 × 5 mm³. The length of each cuboid sample represents 5–10 years. The average time resolution is approximately 350 years.
2.2. Single Particle Analysis by Ice Sublimation

To analyze the embedded impurities, we followed the sublimation-EDS method [Iizuka et al., 2009]. Sample surfaces were decontaminated on a clean bench in the −50°C cold room using a ceramic knife. Approximately 1 g of decontaminated sample was pulverized using a clean ceramic knife and placed on a polycarbonate membrane filter with 0.45 μm diameter pores, which was set in a sublimation chamber. This sublimation chamber was set in a −50°C freezer where clean, dry air (compression air pressure of 0.55 MPa, dew point of −65°C) flowed through at a rate of 15 L min⁻¹ for 100 h.

After sublimation, each filter yielded at least 200 nonvolatile particles exceeding 0.45 μm in diameter. We measured their constituent elements and diameter using a JSM-6360LV (JEOL) SEM (scanning electron microscope) and a JED2201 (JEOL) EDS (energy dispersive X-ray spectroscopy) system. To avoid electrical charging of the filter and to improve accuracy, the filter was coated with a Pt film using magnetron sputtering (MSP-10 Magnetron Sputter) before the SEM-EDS measurement. The accelerating voltage was 20 keV to allow the electron beam to penetrate micrometer-sized particles. The X-ray spectrum of each particle was measured for 45–80 s. To be counted as a nonvolatile particle, a particle had to contain at least one of Na, Mg, Si, Al, S, Cl, K, and Ca, each with an atomic ratio (%) amount at least twice that of the error (%). We also observed C, Cr, Fe, and Pt but interpreted these peaks as artifacts from the membrane filter (C), sample mount (Cr), the stainless steel of the sublimation system (Fe), and filter coating (Pt). Other elements were only rarely detected.

2.3. Chemical Compositions of Single Particles From Their Elemental Distribution

Following Iizuka et al. [2009, 2012a, 2012b], we classified nonvolatile particles into insoluble dust, soluble sulfate salts, and soluble chloride salts as follows. If a particle contained Si, we regarded the particle as insoluble dust (silicate); if the particle had S, we assumed that the particle contained a sulfate salt; if it had Cl, we assumed that the particle had chloride salts. More specifically, a particle containing Ca and S was assumed to have CaSO₄, whereas that with Na and S was assumed to have Na₂SO₄. Any other sulfate salt particle was labeled “other-S.” In the same way, for chloride salts, we assumed NaCl and the other chloride salt (other Cl).

We calculated the molar mass of CaSO₄, Na₂SO₄, and NaCl for each sample using the spectrum ratios of each element. The calculation procedure for the molar masses followed that described in Iizuka et al. [2012a, 2012b]. The moles of Na, Ca, S, and Cl were calculated from the atomic ratios measured in the EDS X-ray spectrum. When a particle has Na and S, the molar mass of Na₂SO₄ is equal to the smaller mass of either Na or S. If [Na] < [S], then [Na₂SO₄] = [Na] (μeq). If [Na] > [S], then [Na₂SO₄] = [S] (μeq). The same procedure applies to [CaSO₄] and [NaCl]. When a particle has Na, Ca, and S, the molar ratio of Na₂SO₄ and CaSO₄ depends on that of Na and Ca as follows.

If [Ca] + [Na] > [S] (μeq),

\[ [\text{CaSO}_4] = \frac{[\text{Ca}]}{([\text{Ca}] + [\text{Na}])} \times [\text{S}] \text{(μeq);} \]

\[ [\text{Na}_2\text{SO}_4] = \frac{[\text{Na}]}{([\text{Ca}] + [\text{Na}])} \times [\text{S}] \text{(μeq);} \]

If [Ca] + [Na] ≥ [S] (μeq), [CaSO₄] = [Ca] (μeq), and [Na₂SO₄] = [Na] (μeq). When a particle has Na, S, and Cl, the molar ratio of Na₂SO₄ and NaCl depends on that of S and Cl as follows.

If [Na] < [S] + [Cl] (μeq),

\[ [\text{Na}_2\text{SO}_4] = [\text{Na}] \times \frac{[\text{S}]}{([\text{S}] + [\text{Cl}]}) \text{(μeq);} \]

\[ [\text{NaCl}] = [\text{Na}] \times \frac{[\text{Cl}]}{([\text{S}] + [\text{Cl}]}) \text{(μeq);} \]

If instead [Na] > [S] + [Cl] (μeq), then [Na₂SO₄] = [S] (μeq) and [NaCl] = [Cl] (μeq).

Uncertainty in the molar masses was calculated as follows. We selected a particle at random. If, for example, it contained Na and S, then we repeatedly (20 times) measured its atomic ratios of Na and S. We then
calculated the ratio of the standard deviation to the average value of the 20 measurements and obtained the coefficient of variation $CV_{\text{NaS}} = 0.20$. For Ca and S, we obtained $CV_{\text{CaS}} = 0.22$, and for Na and Cl, we obtained $CV_{\text{NaCl}} = 0.20$. The uncertainties of the molar ratio of Na$_2$SO$_4$/CaSO$_4$ and NaCl/Na$_2$SO$_4$, hereafter $CV_{\text{ratio}}$, were obtained by error propagation. The $CV_{\text{ratio}}$ for the molar ratio of Na$_2$SO$_4$/CaSO$_4$ was 0.30 and that of NaCl/Na$_2$SO$_4$ was 0.29.

For calculating the molar masses of nonvolatile particles, we regarded each particle as an ellipsoid of revolution around the particle major axis, with major and minor axes taken from the particle shadow area. The error of this assumption was obtained by picking 200 particles at random and then measuring the deviation between their actual shadow area and comparing it to the idealized ellipse shadow area. The results showed that 95% of the particles had areas that differed by less than 20%. From this result, we calculated the error in particle volume. The total uncertainty for the molar ratio of Na$_2$SO$_4$/CaSO$_4$ was 50%, whereas that for NaCl/Na$_2$SO$_4$ was 49%.

2.4. Ion Concentrations

The ion concentrations (Ca$^{2+}$, Na$^+$, SO$_4^{2-}$, Cl$^-$, and NO$_3^-$) of 122 samples from 326.4 m to 579.8 m were analyzed using ion chromatography (Dionex DX-500) at the National Institute of Polar Research. We added these samples to the existing data set of 172 samples of Watanabe et al. [2003b] to make 294 samples. In the SO$_4^{2-}$ data, we identified volcanic-eruption signal spikes ($n = 8$) from the original SO$_4^{2-}$ data ($n = 294$) using the method of Igarashi et al. [2011]. The mean value $M$ and the standard deviation $\sigma$ were calculated using non-sea-salt SO$_4^{2-}$ values, yielding $M = 137.6$ ppb and $\sigma = 64.6$ ppb. We selected eight spikes with values exceeding $M + 2\sigma = 266.7$ ppb. The nssSO$_4^{2-}$ calculation followed the method in Bigler et al. [2006].

Ions fluxes were derived by multiplying the ion concentration with the reconstructed annual snow accumulation. The snow accumulation rate was derived from the $\delta^{18}$O record [Watanabe et al., 2003a] of the Dome Fuji ice core, following the equation in Parrenin et al. [2007], and it had an uncertainty of 17% for the LGM and 5.3% for the Holocene. The average blank contribution to the SO$_4^{2-}$ concentration equaled 1.3% from 25.0 to 16.0 kyr B.P. and 2.1% from 16.0 to 11.0 kyr B.P. For these two periods, the corresponding values were 2.8 and 7.4% for Na$^+$, 5 and 38% for Ca$^{2+}$, and 0.5 and 1.8% for Cl$^-$.

2.5. Salt Inclusions Deduced From Ion Concentrations

The concentrations of CaSO$_4$, Na$_2$SO$_4$, and NaCl inclusions were calculated from the Ca$^{2+}$, Na$^+$, SO$_4^{2-}$, Cl$^-$, and NO$_3^-$ concentrations. We applied three calculation methods (Case I to III) based on previously suggested salt formation processes. The ion-deduced values from Case I to III were examined using salt data from the sublimation-EDS method.

Case I

The Na$^+$ forms NaCl prior to Na$_2$SO$_4$. This case produces NaCl when the Cl$^-$/Na$^+$ ratio is close to the seawater ratio (1.8 [Whitlow et al., 1992]) as Legrand et al. [1988] and Röthlisberger et al. [2003a] suggested. If Cl$^-$/Na$^+$ ≥ 1.8, then

$$[\text{NaCl}] = [\text{Na}^+],$$
$$[\text{Na}_2\text{SO}_4] = 0,$$ and
$$[\text{CaSO}_4] \text{ equals the smaller of } [\text{Ca}^{2+}] \text{ and } [\text{SO}_4^{2-}].$$

If Cl$^-$/Na$^+$ < 1.8 and [Ca$^{2+}$] > [SO$_4^{2-}$], we assume

$$[\text{NaCl}] = [\text{Cl}^-],$$
$$[\text{Na}_2\text{SO}_4] = 0,$$ and
$$[\text{CaSO}_4] = [\text{SO}_4^{2-}].$$

If Cl$^-$/Na$^+$ < 1.8 and [Ca$^{2+}$] < [SO$_4^{2-}$], then,

$$[\text{NaCl}] = [\text{Cl}^-],$$
$$[\text{Na}_2\text{SO}_4] \text{ equals the smaller of } [\text{Na}^+] - [\text{Cl}^-] \text{ and } [\text{SO}_4^{2-}] - [\text{Ca}^{2+}],$$ and
$$[\text{CaSO}_4] = [\text{Ca}^{2+}].$$
Case II

The Ca\(^{2+}\) forms sulfate prior to nitrate and before the Na\(^{+}\) forms sulfate, whereas Na\(^{+}\) forms Na\(_2\)SO\(_4\) prior to NaCl. This case is based on ideas from papers such as Röthlisberger et al. [2003a], Iizuka et al. [2008], and Sakurai et al. [2011]. If [Ca\(^{2+}\)] > [SO\(_4^{2-}\)], we assume the following:

\[
\begin{align*}
\text{[CaSO}_4\text{]} &= \text{[SO}_4^{2-}\text{]/C}_0, \\
\text{[Na}_2\text{SO}_4\text{]} &= 0, \text{ and} \\
\text{[NaCl]} &= \text{[Na}^+\text{]} + \text{[Ca}^{2+}\text{]} - \text{[SO}_4^{2-}\text{]} - \text{[NO}_3^-\text{].}
\end{align*}
\]

When this gives [NaCl] > [Cl\(^-\)], we assume that [NaCl] = [Cl\(^-\)], and when this gives [NaCl] ≤ 0, we assume that [NaCl] = 0.

If [Ca\(^{2+}\)] < [SO\(_4^{2-}\)] and [Ca\(^{2+}\)] + [Na\(^{+}\)] > [SO\(_4^{2-}\)] + [NO\(_3^-\)], we assume that

\[
\begin{align*}
\text{[CaSO}_4\text{]} &= \text{[Ca}^{2+}\text{]/C}_0\text{[NO}_3^-\text{],} \\
\text{[Na}_2\text{SO}_4\text{]} &= \text{[SO}_4^{2-}\text{]} + \text{[NO}_3^-\text{]/C}_0\text{[Ca}^{2+}\text{]}, \text{ and} \\
\text{[NaCl]} &= \text{[Na}^+\text{]} + \text{[Ca}^{2+}\text{]} - \text{[SO}_4^{2-}\text{]} - \text{[NO}_3^-\text{].}
\end{align*}
\]

Similarly, when this gives [NaCl] > [Cl\(^-\)], we assume that [NaCl] = [Cl\(^-\)], but when this gives [NaCl] ≤ 0, we assume that [NaCl] = 0.

If [Ca\(^{2+}\)] + [Na\(^{+}\)] < [SO\(_4^{2-}\)], we assume that all of the Ca\(^{2+}\) and Na\(^{+}\) are in the form of sulfates:

\[
\begin{align*}
\text{[CaSO}_4\text{]} &= \text{[Ca}^{2+}\text{],} \\
\text{[Na}_2\text{SO}_4\text{]} &= \text{[Na}^+\text{],} \text{ and} \\
\text{[NaCl]} &= 0.
\end{align*}
\]

Case III

The Ca\(^{2+}\) forms nitrate prior to sulfate. This case is based on an implication of Röthlisberger et al. [2000]. If [Ca\(^{2+}\)] > [NO\(_3^-\)] + [SO\(_4^{2-}\)], we assume that

\[
\begin{align*}
\text{[CaSO}_4\text{]} &= \text{[SO}_4^{2-}\text{]/C}_0, \\
\text{[Na}_2\text{SO}_4\text{]} &= 0, \text{ and} \\
\text{[NaCl]} &= \text{the smaller of [Na}^+\text{] and [Cl}^-\text{].}
\end{align*}
\]

If [Ca\(^{2+}\)] > [NO\(_3^-\)] and [Ca\(^{2+}\)] + [Na\(^{+}\)] > [NO\(_3^-\)] + [SO\(_4^{2-}\)], we assume that

\[
\begin{align*}
\text{[CaSO}_4\text{]} &= \text{[Ca}^{2+}\text{] - [NO}_3^-\text{],} \\
\text{[Na}_2\text{SO}_4\text{]} &= \text{[SO}_4^{2-}\text{] + [NO}_3^-\text{] - [Ca}^{2+}\text{],} \text{ and} \\
\text{[NaCl]} &= \text{[Na}^+\text{] + [Ca}^{2+}\text{] - [SO}_4^{2-}\text{] - [NO}_3^-\text{].}
\end{align*}
\]

When this gives [NaCl] > [Cl\(^-\)], we assume that [NaCl] = [Cl\(^-\)].

If [Ca\(^{2+}\)] > [NO\(_3^-\)] and [Ca\(^{2+}\)] + [Na\(^{+}\)] < [NO\(_3^-\)] + [SO\(_4^{2-}\)], we assume that

\[
\begin{align*}
\text{[CaSO}_4\text{]} &= \text{[Ca}^{2+}\text{] - [NO}_3^-\text{],}
\end{align*}
\]
If $[Ca^{2+}] + [Na^+] < [NO_3^{-}]$, we assume that all of the $Ca^{2+}$ and $Na^+$ are in the form of nitrate:

- $[CaSO_4] = 0$
- $[Na_2SO_4] = 0$
- $[NaCl] = 0$

If $[Ca^{2+}] < [NO_3^{-}]$ and $[Ca^{2+}] + [Na^+] < [NO_3^{-}] + [SO_4^{2-}]$, we assume that:

- $[CaSO_4] = 0$
- $[Na_2SO_4] = [Na^+] + [Ca^{2+}] - [NO_3^{-}]$
- $[NaCl] = 0$

If $[NaCl] > [Cl^{-}]$, we assume that $[NaCl] = [Cl^{-}]$.

In a later section, we propose a fourth method, Case IV.

### 3. Results and Discussion

#### 3.1. Comparison of Sulfate Salt Compositions Using the Sublimation-EDS and Micro-Raman Methods

In total, we analyzed 11,262 nonvolatile particles. Figure 1 shows representative particles of the warm and cold stages. $CaSO_4$, $Na_2SO_4$, and $NaCl$ are the dominant sulfate and chloride salts during the last termination in the Dome Fuji ice core, so we focused on these salts. To evaluate the abundance of sulfate salts obtained from the sublimation-EDS method, we compared the number ratio of $Na_2SO_4/CaSO_4$ obtained from the sublimation-EDS method with that of the micro-Raman method [Sakurai et al., 2011].

The micro-Raman method can directly measure the sulfate composition of micron-sized salt particles in ice. Except for the data point at 24.7 kyr B.P., the number ratio of $Na_2SO_4/CaSO_4$ from the sublimation-EDS method agrees with that of the micro-Raman method [Sakurai et al., 2011]. The micro-Raman method can directly measure the sulfate composition of micron-sized salt particles in ice. The sublimation-EDS method gave 0.92 ± 0.40 from 25.0 to 17.3 kyr B.P., whereas the micro-Raman method gave 0.04 at 24.7 kyr B.P. and 0.79 at 19.3 kyr B.P. The average ratio from the sublimation-EDS method after 16.8 kyr B.P. was 3.27 ± 1.76. For the micro-Raman method, the ratios at 16.8, 14.3, 12.9, and 11.2 kyr B.P. were 1.53, 3.91, 4.09, and 5.40, respectively. Thus, the sublimation-EDS method reconstructs the particle number of $Na_2SO_4$ and $CaSO_4$ with the same level of accuracy as the micro-Raman method.

This result suggests that chemical reactions between acids and salts are unlikely during the sublimation process. The acids ($H_2SO_4$, $HNO_3$, and $HCl$) should be preserved in ice cores [Legrand et al., 1988; Iizuka et al., 2008]. Under sublimation conditions ($-50^\circ C$, 0.55 MPa), $H_2SO_4$ remains liquid and $HNO_3$ remains solid, whereas $HCl$ becomes a volatile gas [Ohno et al., 2005]. The sublimation process takes approximately 100 h, during which time the $H_2SO_4$ has plenty of time to flow through the filter. We measured the filter directly at random and only detected $C$, $O$, Pt, Cr, and Fe. With no $S$ detected on the filter, the salt compounds had little opportunity to react with $H_2SO_4$.
3.2. Major Chemical Compositions of Nonvolatile Particles

Particles containing Si are assumed to contain silicate, a major component of insoluble particles [Iizuka et al., 2009]. Most of the nonvolatile particles here contained Si. Between 25.0 and 16.6 kyr B.P., 94 ± 3% of particles contained Si (Figure 3). When the dust concentration becomes about half of the LGM level at around 16.6 kyr B.P. [Fujii et al., 2003; Röthlisberger et al., 2003b], the ratio starts to decrease. The ratio in 16.6–11.0 kyr B.P. showed large variability (29–96%) with an average ratio of 72 ± 16%. The significant decrease in dust concentration from the LGM increased the ratio of nonvolatile particle without Si (mainly soluble particle).

In examining 6075 sulfate and chloride particles, we found that Na$_2$SO$_4$ accounts for 42.6%, CaSO$_4$ for 20.9%, and NaCl for 23.1% of all the sulfate and chloride particles (Figure 4a). The time series of Na$_2$SO$_4$, CaSO$_4$, and NaCl particles without Si clearly showed that their fraction increases after 16.3 kyr B.P.
This change occurs when the number ratio of Si-containing particles decreases (Figure 3). Between 25.0 and 16.6 kyr B.P., 91 ± 4% of the three salts included Si. Between 16.3 and 11.0 kyr B.P., that fraction decreased to 56 ± 20%. When considering the salt type, the non-Si salt with the largest fraction was Na$_2$SO$_4$. These trends indicate that the opportunity for atmospheric aerosols such as sea salt to encounter dust decreases as the amount of dust decreases.

The salt distribution can be divided into two time periods: 25.0–16.6 kyr B.P. and 16.3–11.0 kyr B.P. (Figure 4c). For 25.0–16.6 kyr B.P., most particles have 20–55% CaSO$_4$, 20–40% Na$_2$SO$_4$, and 20–40% NaCl. That is, the fractions during this period are all approximately one third (CaSO$_4$ is 36 ± 12, Na$_2$SO$_4$ is 35 ± 9, and NaCl is 28 ± 8%). However, for 16.3–11.0 kyr B.P., the particles have 10–30% CaSO$_4$, 45–80% Na$_2$SO$_4$, and 5–30% NaCl (with four exceptions). That is, compared to the older period, the NaCl fraction decreases, the CaSO$_4$ fraction decreases (more than NaCl), and the Na$_2$SO$_4$ fraction shows a large increase. Most of the CaSO$_4$ and NaCl fraction lies below 30% with the Na$_2$SO$_4$ fraction above 40%. The four exceptions at 14.3, 12.3, 12.0, and 11.2 kyr B.P. have 9–21% CaSO$_4$, 35–43% Na$_2$SO$_4$, and 38–50% NaCl, that is, a lower Na$_2$SO$_4$ fraction and a higher NaCl fraction.

Figure 5a shows the molar ratio of Na$_2$SO$_4$/CaSO$_4$ calculated from the sublimation result. The ratio starts low at 0.66 ± 0.83 during 25.0–18.0 kyr B.P. (right side of plot), increases between 18.0 and 16.0 kyr B.P., and then stays high at 5.05 ± 2.35 through 11.0 kyr B.P. At 16.8 kyr B.P., the ratio changes from below 1 (CaSO$_4$ > Na$_2$SO$_4$) to above 1 (CaSO$_4$ < Na$_2$SO$_4$), showing the same trend as that found previously for the number ratio (Figure 2). This result indicates that the primary sulfate salt changes from CaSO$_4$ to Na$_2$SO$_4$ at 16.8 kyr B.P.

Figure 5b shows the analogous result for NaCl/Na$_2$SO$_4$. The ratio is high during the LGM, but then it decreases between 17.3 and 16.3 kyr B.P. After 16.3 kyr B.P., the ratio stays low. The average ratio decreases fivefold, from 2.77 ± 1.62 during 25.0–17.3 kyr to 0.54 ± 0.50 during 16.3–11.0 kyr B.P. Spikes occur at 12.3, 12.0, 11.2, and 11.1 kyr B.P. These spikes show NaCl/Na$_2$SO$_4$ to have high variability after 12.3 kyr B.P. The high NaCl/Na$_2$SO$_4$ variability is likely linked to an increase in the seasonal contribution of NaCl to the atmospheric aerosol in winter during this period. (The seasonal effect is discussed in the next section.)

The origin of Ca$^{2+}$ is gypsum (CaSO$_4$) and CaCO$_3$. CaCO$_3$ is neutralized in the atmosphere by H$_2$SO$_4$ during its transport to inland Antarctica [Anklina et al., 1997; Tschumi and Stauffer, 2000; Kawamura et al., 2003]. Later, Sakurai et al. [2011] showed that the concentration of Ca$^{2+}$ correlates strongly with the frequency of CaSO$_4$ and suggested that most Ca$^{2+}$ ion forms CaSO$_4$ at every depth of the last termination. The Ca$^{2+}$ concentration, therefore, can be regarded as the CaSO$_4$ concentration. From the Na$_2$SO$_4$/CaSO$_4$ ratio, we used the CaSO$_4$ flux (Figure 6b) to deduce the Na$_2$SO$_4$ flux (Figure 6c). As shown in Figure 6d, the total sulfate salt flux (CaSO$_4$ plus Na$_2$SO$_4$) has high values from 25 kyr B.P., equaling 6.5 ± 1.6 mg m$^{-2}$ yr$^{-1}$ at 18.0 kyr B.P. Then, from 18.0 to 14.7 kyr B.P., CaSO$_4$ decreases as Na$_2$SO$_4$ increases, resulting in a moderate decrease.
sulfate salt flux decrease. After that, the flux decreases more, reaching a low value of 2.6 ± 0.9 mg m⁻² yr⁻¹ at 11.0 kyr B.P.

As found in the last three glacial cycles [Iizuka et al., 2012b], the decrease in the sulfate salt flux inversely correlates with δ¹⁸O over millennial timescales (Figure 7). The squared correlation coefficient is $R^2 = 0.41$ ($p < 0.001$). This contrasts with the SO₄²⁻ flux, which showed no clear correlation with δ¹⁸O (Figure 6e and 7).

Sulfate salt aerosols are a key component of CCN in the atmosphere [Köhler, 1936; Petters and Kreidenweis, 2007], which lead to increased solar scattering that cools Earth's climate [IPCC, 2007, 2013]. The reduction in the sulfate salt flux, therefore, may have contributed to the last deglacial warming in inland Antarctica.

### 3.3. Validity of Ion-Deduced Sulfate and Chloride Salts

Comparisons between the sublimation-EDS method and Case I of the ion-deduced method are plotted in Figures 8a and 8b. For the Na₂SO₄/CaSO₄ ratio, Figure 8a shows the slope as 0.35 with a low correlation ($R^2 = 0.19$), whereas Figure 8b shows the NaCl/Na₂SO₄ ratio as 9.78 with a low correlation ($R^2 = 0.24$). The Case I assumption leads to too much NaCl over the entire period. The results of the micro-Raman method [Sakurai et al., 2011] and the sublimation-EDS method showed that Na₂SO₄ exists not only after 16.8 kyr B.P. but before as well; however, the estimated values from Case I do not show the Na₂SO₄ between 25.0 and 16.8 kyr B.P. that was revealed in both the sublimation-EDS and the micro-Raman methods. Similar to that found at Dome C [Röthlisberger et al., 2003a], the value of Cl⁻/Na⁺ of Dome Fuji of 16–25 kyr B.P. is close to the seawater ratio (Figure 6g). This implies that NaCl has not reacted with sulfuric acid or nitric acid. However, the data from the sublimation-EDS and the micro-Raman methods suggest that the assumption about Na⁺, in which Na⁺ forms NaCl when the Cl⁻/Na⁺ ratio is near the seawater ratio, is wrong. Here the Cl⁻/Na⁺ ratio is close to the seawater ratio between 25.0 and 16.8 kyr B.P., yet some Na⁺ must form Na₂SO₄ instead of NaCl. The presence of Na₂SO₄ indicates the possible presence of HCl and/or other chloride salts in this period. We cannot detect HCl because HCl volatilizes during the sublimation, but we found Cl-containing particles (e.g., with MgCl₂). The results, therefore, suggest that the seawater Cl⁻/Na⁺ ratio does not necessarily indicate that NaCl has not reacted with sulfuric acid.

In contrast, Case II correlates well with the sublimation-EDS method. For the molar ratios of Na₂SO₄/CaSO₄, the slope is 0.96 with a high correlation ($R^2 = 0.86$) (Figure 8c). This nearly 1:1 relationship suggests that Case II deduces CaSO₄ and Na₂SO₄ accurately. For NaCl/Na₂SO₄, the slope is 0.89 with a high correlation.
$R^2 = 0.50$ (Figure 8d). However, Case II underestimates the $[\text{NaCl}]$ values in 16.3–11.0 kyr B.P., giving a value of zero because $[\text{SO}_4^{2-}]$ exceeds the sum of $[\text{Ca}^{2+}]$ and $[\text{Na}^+]$. Thus, Case II poorly reconstructs NaCl during the warm period.

Case III predicts CaSO$_4$ concentrations that are too low, which makes the Na$_2$SO$_4$ concentration too high and the NaCl concentrations too low. As a result, the molar ratio of Na$_2$SO$_4$/CaSO$_4$ is too high and that of NaCl/Na$_2$SO$_4$ is too low. The slope for Na$_2$SO$_4$/CaSO$_4$ is 44.0 with $R^2 = 0.06$ (Figure 8e) and that for NaCl/Na$_2$SO$_4$ is 0.21 with $R^2 = 0.54$ (Figure 8f). Thus, Case III is not supported by the salt-inclusion data from the sublimation-EDS method.

We now propose a modification of Case II, to be called Case IV. The low values of NaCl in the warm period from Case II may be related to the seasonality of atmospheric aerosol. Aerosol observations in inland Antarctica showed that the activity of phytoplankton-producing SO$_4^{2-}$ dominates in summer, whereas sea-salt aerosol dominates in winter [e.g., Hara et al., 2004; Preunkert et al., 2008; Udisti et al., 2012]. A certain amount of the winter sea salt, therefore, would not encounter the summer marine biogenic sulfate and thus not fully react in the atmosphere. The 5–10 year averaging of the ion balance method would then overestimate the reaction between NaCl and SO$_4^{2-}$.

**Figure 7.** Correlations of sulfate salt and $\text{SO}_4^{2-}$ fluxes to $\delta^{18}\text{O}$. The linear fitting line for sulfate salt is $F_{\text{SALT}} = -0.52 \delta^{18}\text{O} - 25.6$ with $R^2 = 0.41$ ($n = 35$, $p < 0.001$) (Of the 39 particle samples, four had no corresponding ion measurement at the same depth).

**Figure 8.** Comparison of ion-deduced methods to the sublimation-EDS method. (a, c, e, and g) The molar ratio $\text{Na}_2\text{SO}_4$/CaSO$_4$ (b, d, f, and h) NaCl/Na$_2$SO$_4$. Case I ion-deduced method (Figures 8a and 8b). Case II (Figures 8c and 8d). Case III (Figures 8e and 8f). Case IV (Figures 8g and 8h). The solid lines are the linear fitting lines. Dotted lines mark the 1:1 relation (Number of data points $n = 35$ for Figures 8a–8c and 8g and $n = 30$ for Figures 8d–8f and 8h. Of the 39 particle samples, four had no corresponding ion measurement at the same depth and five had an anomalous value of NO$_3^-$.)

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Assuming that the chemical reaction of $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$ occurred completely within each single month, we calculated the monthly $Na_2SO_4$ and NaCl concentrations using the monthly concentrations of $Na^+$ and $SO_4^{2-}$. The $Na^+$ and $SO_4^{2-}$ concentrations were measured at Dome C in 2006 [Preunkert et al., 2008]. The estimated summer (December–March) concentrations are 0.17 nEq/m$^3$ for $Na_2SO_4$ and zero for NaCl. In winter (April–November), concentrations of $Na_2SO_4$ and NaCl are 0.24 and 0.09 nEq/m$^3$, respectively. The annual mean values, based on the sum of monthly estimates, are 0.22 nEq/m$^3$ for $Na_2SO_4$ and 0.07 nEq/m$^3$ for NaCl. Thus, by including the seasonality, we obtained a molar equivalent ratio of NaCl to $Na^+$ of 0.23 instead of the zero value we obtained by ignoring seasonality. We use this finding for Case IV.

Case IV
This follows Case II, except that we assume that 23% per year of $Na^+$ exists as NaCl in 16.3–11.0 kyr B.P.

If $[Ca^{2+}] > [SO_4^{2-}]$, then $[CaSO_4] = [SO_4^{2-}]$, $[Na_2SO_4] = 0$, and $[NaCl] = [Na^+] + [Ca^{2+}]$ – $[SO_4^{2-}]$ – $[NO_3^-]$. When this gives $[NaCl] > [Cl^-]$, we assume that $[NaCl] = [Cl^-]$, and when this instead gives $[NaCl] \leq 0$, then $[NaCl] = 0$.

If $[Ca^{2+}] < [SO_4^{2-}]$ and $[Ca^{2+}] + [Na^+] > [SO_4^{2-}]$, we assume that $[CaSO_4] = [Ca^{2+}]$, $[Na_2SO_4] = [SO_4^{2-}]$ – $[Ca^{2+}]$, and $[NaCl] = [Na^+] + [Ca^{2+}]$ – $[SO_4^{2-}]$ – $[NO_3^-]$. When this gives $[NaCl] > [Cl^-]$, we assume that $[NaCl] = [Cl^-]$, and when this instead gives $[NaCl] \leq 0$, we set $[NaCl] = 0$.

If $[Ca^{2+}] + [Na^+] < [SO_4^{2-}]$ (16.3–11.0 kyr B.P.), then $[CaSO_4] = [Ca^{2+}]$, $[Na_2SO_4] = [Na^+] – 0.23[Na^+]$, and $[NaCl] = 0.23[Na^+]$.

The resulting NaCl/$Na_2SO_4$ ratios from Case IV fit the sublimation-EDS method (Figure 8h) better than those from Case II. Both the slope and the $R^2$ value have improved. For $Na_2SO_4/CaSO_4$, the method also agrees well with the sublimation-EDS method, with a regression slope of $0.84 \pm 0.07$ and $R^2 = 0.82$ (Figure 8g). Thus,
the Case IV method reproduces not only CaSO₄ and Na₂SO₄ but also the NaCl concentration. Additionally, the agreement between Case IV and the sublimation-EDS results suggests that winter atmospheric aerosols are well preserved for at least the most recent 16 kyr.

The CaSO₄, Na₂SO₄, and NaCl fluxes based on Case IV are shown in Figure 9. The CaSO₄ flux shows the high value of 3.1 ± 0.8 mg m⁻² yr⁻¹ during 25.0–18.0 kyr B.P., but then it decreases dramatically around 18.0–16.0 kyr B.P. After that, the flux stays low at 0.4 ± 0.2 mg m⁻² yr⁻¹. In contrast, the Na₂SO₄ flux of 1.6±0.4 mg m⁻² yr⁻¹ slightly increases from 20.0 kyr B.P., reaching a high value of 2.8±0.4 mg m⁻² yr⁻¹ around 16.0 kyr B.P. After 16.0 kyr B.P., this flux decreases with high variability, then reaches the low value of 1.6 ± 0.4 mg m⁻² yr⁻¹ at 11.0 kyr B.P. The NaCl flux has a relatively high value with high variability (0.7 ± 0.6 mg m⁻² yr⁻¹) until 20.0 kyr B.P. Then, this flux becomes low and stable (0.4 ± 0.2 mg m⁻² yr⁻¹).

Consider the total sulfate salt flux (CaSO₄ plus Na₂SO₄), in the LGM ice, it has a value of 5.3 ± 0.6 mg m⁻² yr⁻¹ (Figure 9d) and starts to decrease around 18.0 kyr B.P. After that, the flux decreases moderately, reaching the low value of 1.8 ± 0.4 mg m⁻² yr⁻¹ at 11.0 kyr B.P. This sulfate salt flux also correlates inversely with δ¹⁸O (Figure 10). The squared correlation coefficient is $R^2 = 0.71$ ($p < 0.001$), which is stronger than that from the previous ion-deduced method based on Case II ($R^2 = 0.56$, $p < 0.001$). This stronger correlation suggests that sulfate salt aerosols likely contributed to the last deglacial warming of inland Antarctica by reducing the aerosol indirect effect.

4. Conclusion

We presented the chemical compositions of nonvolatile particles during the last termination in the Dome Fuji ice core with a 350 year resolution. The results obtained using the sublimation-EDS method agreed well with the existing record obtained by Raman spectroscopy, indicating that the sublimation-EDS method for extracting nonvolatile particles does not suffer from contamination.

Using the sublimation-EDS method, the major components of the insoluble particles were found to be silicate, whereas that of the soluble particles were CaSO₄, Na₂SO₄, and NaCl salts. Starting with the oldest ice, the dominant sulfate salt changed at 16.8 kyr B.P. from CaSO₄, a glacial type, to Na₂SO₄, an interglacial type. The derived sulfate salt flux (CaSO₄ plus Na₂SO₄) began at the high value of 6.1 ± 1.6 mg m⁻² yr⁻¹ and then started to decrease from 18.0 kyr B.P. reaching a low value of 1.6 mg m⁻² yr⁻¹ at 11.0 kyr B.P. The decrease in the sulfate salt flux correlated inversely with δ¹⁸O with millennial timescales. This contrasts with the SO₄²⁻ flux, which showed no clear correlation with δ¹⁸O. The reduction in the sulfate salt flux likely contributed to the last deglacial warming in inland Antarctica by reducing the aerosol indirect effect.
In contrast to previous studies based on ion concentrations, the sublimation-EDS method detected NaCl in 16.3–11.0 kyr B.P. The presence of NaCl in this period suggests that winter atmospheric aerosols were preserved in the ice. In response to this finding, we proposed a new ion-deduced method by assuming that 23% per year of Na⁺ exists as NaCl in Dome Fuji ice when the ionic balance satisfies \([\text{Ca}^{2+}] + [\text{Na}^+] < [\text{SO}_4^{2-}]\). The molar ratios of NaCl/Na₂SO₄ and Na₂SO₄/CaSO₄ estimated using the new ion-deduced method agreed well with that from the sublimation-EDS method. The agreement indicates that the new ion-deduced method reproduces the CaSO₄, Na₂SO₄, and NaCl concentrations better than previous ion-deduced methods. The sulfate salt flux from the new ion-deduced method has an inverse correlation with δ¹⁸O that is stronger than that from the previous ion-deduced method. This result strongly suggests that sulfate salt aerosols contributed to the last deglacial warming of inland Antarctica by reducing the aerosol indirect effect.

Acknowledgments
We thank all members of the Dome Fuji drilling team, all participants in the Japanese Antarctic Research Expedition and Ice Core Consortium for Dome Fuji activities, S. Fujita of the National Institute of Polar Research for data revising, H. Ohno of the Kitami Institute of Technology for useful comments, M. Furusaki of the Institute of Low Temperature Science for help with EDS methods. The sulfate salt

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