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**Chemical compositions of past soluble aerosols
reconstructed from Greenland and Antarctic ice cores**

南極及びグリーンランド氷床コアから復元した過去の水溶性エアロゾルの化学組成

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ABSTRACT

Aerosols play an important role in the global climate balance, and therefore they could be important in climate change. Chemical compositions of aerosols are one of the important information for understanding the role of aerosols. Therefore, it is required to clear spatial and temporal distributions of chemical compositions of aerosols. Polar ice cores preserve past atmospheric aerosols, which is a useful proxy for understanding the interaction between climate changes and atmospheric aerosols. One useful technique for reconstructing past soluble aerosols from ice cores is the determination of dissolved ion species. For instance, Na^+ and Ca^{2+} are the major cations of both Greenland and Antarctic ice cores. The Na^+ originates from sea-salt (NaCl), and the Ca^{2+} originates from terrestrial materials (CaCO_3 and CaSO_4). The NaCl and CaCO_3 react with sulfuric acid (H_2SO_4), and change to Na_2SO_4 and CaSO_4 . It has been clearly known that the contribution of terrestrial aerosols is higher in the glacial period, whereas that of sea-salt aerosols is higher in the interglacial period. However, since salts and acids melt into ions, chemical compositions of soluble aerosols in the ice cores have not been cleared. To clarify the temporal variations in the chemical compositions of past soluble aerosols, and the interaction between past soluble aerosols (sulfate-salt aerosols) and temperature changes, this study investigated chemical compositions of soluble particles preserved in the Greenland and Antarctic ice cores by focusing on the last termination, the most recent climate transition.

The ice core samples are selected from the sections from the last termination (the Last Glacial Maximum (LGM) to Holocene) of the Dome Fuji and Dome C (inland Antarctica) ice cores, and the sections of the last interglacial period to Holocene of the Greenland NEEM ice core. Using the ice-sublimation method, soluble salt particles were extracted without melting. Chemical components of extracted particles were analysed by scanning electron microscope and energy dispersive spectroscopy, and micro-Raman spectroscopy.

The major components of soluble salts particles in the Antarctic ice cores (Dome Fuji and Dome C) are CaSO_4 , Na_2SO_4 and NaCl . The CaSO_4 and NaCl fractions were high in the first half of the last termination, whereas the Na_2SO_4 fraction is high in the latter half of the last termination. The major components of soluble salts particles in the NEEM ice core are CaCO_3 , CaSO_4 , NaCl and Na_2SO_4 . The fractions of CaCO_3 , CaSO_4 and NaCl were high in LGM, whereas those of NaCl and Na_2SO_4 were high in Holocene.

The changes in the salt compositions in Antarctica are mainly controlled by concentration of terrestrial material (Ca^{2+}). In the first half of the last termination, most of the terrestrial material (CaCO_3) reacted with H_2SO_4 but some of sea-salt (NaCl) did not react with H_2SO_4 due to high Ca^{2+} concentration. As a result, the CaSO_4 and NaCl fractions were high in this period. In the latter half of

the last termination, reaction of NaCl with H₂SO₄ enhanced due to decreased in the Ca²⁺ concentration. As a result, Na₂SO₄ fraction was high in the latter half of the last termination.

The changes in the salt compositions in Greenland are also mainly controlled by Ca²⁺ concentration. In the LGM, some of CaCO₃ reacted, but some of CaCO₃ and most of NaCl did not react with H₂SO₄ due to too high Ca²⁺ concentration. As a result, CaCO₃, CaSO₄ and NaCl fractions were high in the LGM. In the Holocene, NaCl sulfatization increased due to reduction of Ca²⁺ concentration. However, some of NaCl was not sulfatized due to different seasonality of NaCl and H₂SO₄, and increased NH₄⁺ inputs originate from continental biogenic emissions. As a result, Na₂SO₄ and NaCl fractions were high in the Holocene.

Using fractions of salt compositions derived from the sublimation method and ion concentrations, the CaCO₃, CaSO₄, NaCl, Na₂SO₄ and sulfate-salt fluxes of the Dome Fuji, Dome C and NEEM ice cores were estimated. The fluxes of CaCO₃, CaSO₄ and NaCl of the three ice cores in the LGM are significantly higher than in the Holocene, whereas Na₂SO₄ fluxes of the three ice cores are not changed from the LGM to the Holocene. The sulfate-salt flux in the NEEM ice core is relatively high in Greenland cold climate stages, whereas the flux is relatively low in Greenland warm climate stages. In Antarctica, the sulfate-salt flux decreases in Antarctic warming phases, whereas the flux stops decreasing in Antarctic cooling phases. The changes in sulfate-salt fluxes of three ice cores have significant inverse correlations with temperature changes in each three sites, respectively. The production of sulfate-salt was regulated not by SO₄²⁻ which mainly originates from oceanic phytoplankton, but by physical process of oceanic and atmospheric systems. Sulfate-salt aerosols are a key component of cloud condensation nuclei in the atmosphere, which lead to increased solar scattering that cools Earth's climate. The reduction in the sulfate-salt flux may have contributed to the last deglacial warming both in inland Antarctica and Greenland.

The above achievements are new knowledge for the interpretation of ice core records and for the clarification of the role of the soluble aerosols for climate changes, which have not been obtained by traditional ice core studies of soluble aerosols (ion concentrations).

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CHAPTER 1

1 Introduction

1.1 Reconstruction of paleoclimate by polar ice cores

Paleoclimate data are highly important to understand the Earth system and to forecast the future climate. Paleoclimate data record Earth system feedbacks on time scales much longer than what humans have been recording. Also, paleoclimate data record climatic transitions between different climate stages, including abrupt events. Therefore, recent climates changes, and the questions whether or not they are unusual, can be evaluated by comparison with paleoclimate data [IPCC, 2013].

The Quaternary Period is the most recent of the three periods of the Cenozoic Era in the geologic time scale (2.588 million years before present; Myr BP) [Cohen et al., 2013]. The Quaternary Period is divided into two epochs: the Pleistocene (2.588 Myr BP to 11.7 thousand years before present; kyr BP) and the Holocene (around 11.7 kyr BP to today). The last 800 kyr of the Quaternary Period are characterized by growth and reduction of Northern Hemisphere ice sheets with approximately 100 kyr periodicity [Denton et al., 2010; Abe-Ouchi et al., 2013]. The 100-kyr cycle is essentially produced by eccentricity modulation of the precession amplitude through changes in summer insolation [Abe-Ouchi et al., 2013].

Polar ice cores are excellent paleoclimate archives that can reconstruct past climate changes for the last 800 kyr. Ice cores have unique characteristics that allow reconstructing the past atmospheric environment. The year-after-year accumulation of ice on the polar ice sheets creates paleoclimate records. Polar ice reflects the environment at the time of deposition in numerous ways. The isotopic composition of the ice provides long and detailed proxy records of past temperature [e.g., Dansgaard, 2004]. Bubbles preserve trace gases such as CO₂ and CH₄ [e.g., Cuffey and Paterson, 2010]. Also, atmospheric aerosols are trapped in the ice. The CO₂ and aerosols are not triggers for the 100 kyr glacial-interglacial cycle, but they played a role in adjusting the amplitude of temperature changes [IPCC, 2007; Abe-Ouchi et al., 2013].

About 50 years ago, the first Greenland deep ice core was drilled at Camp Century, Northwest Greenland (77°11'N, 61°07' W) in 1966 [Hansen and Langway, 1966]. Two years later, the first Antarctic deep ice core was drilled at Byrd Station, West Antarctica (80°01'S, 119°31'W) [Gow et al., 1968]. In the following 50 years, numerous ice core drilling project have been conducted in the Greenland and Antarctic ice sheets, and a lot of paleoclimate proxies have been obtained (Figure 1). High resolution information can be reconstructed from Greenland ice cores due to higher accumulation rates compared to inland Antarctica. For instance, about 100 kyr paleoclimate records have been reconstructed from as the Renland [Hansson, 1994], GRIP [Dansgaard et al., 1993], GISP2 [Groote et al., 1993] NGRIP [NGRIP community members, 2004], and NEEM [NEEM community members, 2013] ice cores in Greenland. Antarctic ice cores preserve paleoclimate records for much longer periods compared to Greenland ice cores. Many deep ice cores also have been drilled and investigated; for instance, the Vostok [Petit et al., 1999], Dome Fuji [Watanabe et al., 2003a], Dome C [EPICA, 2004], EDML [EPICA, 2006], Talos Dome [Stenni et al., 2011], and WAIS Divide [Marcott et al., 2014] ice cores (Figure 1).

This study focuses on the NEEM ice core from the Greenland ice sheet, and the Dome Fuji and Dome C ice cores from the East Antarctic ice sheet. The NEEM deep ice core was drilled in North-West Greenland (77.45°N, 51.06°W, 2,450 m a.s.l) in 2011. The North Greenland Eemian Ice Drilling - NEEM - is an international ice core research project aimed at retrieving an ice core reaching back through the previous interglacial period. The site has an ice thickness of 2542 m of which 2540 m have been drilled [NEEM community's website]. The current mean annual surface temperature is -29°C , and the snow accumulation rate is 20 cm w.e. a^{-1} . Since the deep ice (below 2206.7 m) was folded and the stratigraphy was disrupted, temperature reconstruction of folded section was tricky, but the ice holds an almost full record of the previous interglacial period [NEEM community members, 2013].

The Japanese Antarctic Research Expedition drilled two deep ice cores at Dome Fuji station in Dronning Maud Land, East Antarctica (77°19' S, 39°42' E) in 1996 and 2007. The Dome Fuji ice core aims at clarifying the present and past glaciological and climate conditions of the Antarctic Ice Sheet in East Dronning Maud Land [Watanabe et al., 1997a, 1997b]. The Dome Fuji station is located at the second highest summit area of the Antarctic ice sheet. The current mean annual surface temperature is -54.3°C [Japan Meteorological Agency, 1996–1998], and the snow accumulation rate is $2.5 \pm 1.0\text{ cm w.e.a}^{-1}$. The first core is 2503 m long and covers the past 340 kyr [Watanabe et al., 2003a], and the second core is 3035 m long and covers the past 720 kyr [Motoyama, 2007].

The European Project for Ice Coring in Antarctica (EPICA), which is a consortium of laboratories and Antarctic logistics operators from ten nations, drilled a deep ice core (3190 m) at the Dome C site in East Antarctica ($75^{\circ}06' \text{ S}$, $123^{\circ}21' \text{ E}$, 3223m a.s.l.) in 2004. The Dome C ice core aims at producing a record of the longest time period possible. The site has an ice thickness of $3309 \pm 22 \text{ m}$ of which 3139 m have been drilled [EPICA, 2002]. The current mean annual surface temperature is -54.5°C , and the snow accumulation rate is $2.5 \text{ cm w.e.a}^{-1}$. The Dome C ice core provides a climate record for the past 800 kyr [EPICA, 2004].

1.2 Temperature changes in Greenland and Antarctica

The stable water isotope records of Greenland and Antarctic ice cores provide detailed proxy records of past temperatures. From the Antarctic records, an extremely strong 100-kyr glacial-interglacial cycle has been found for the last 800 kyr [EPICA, 2004]. A major climatic

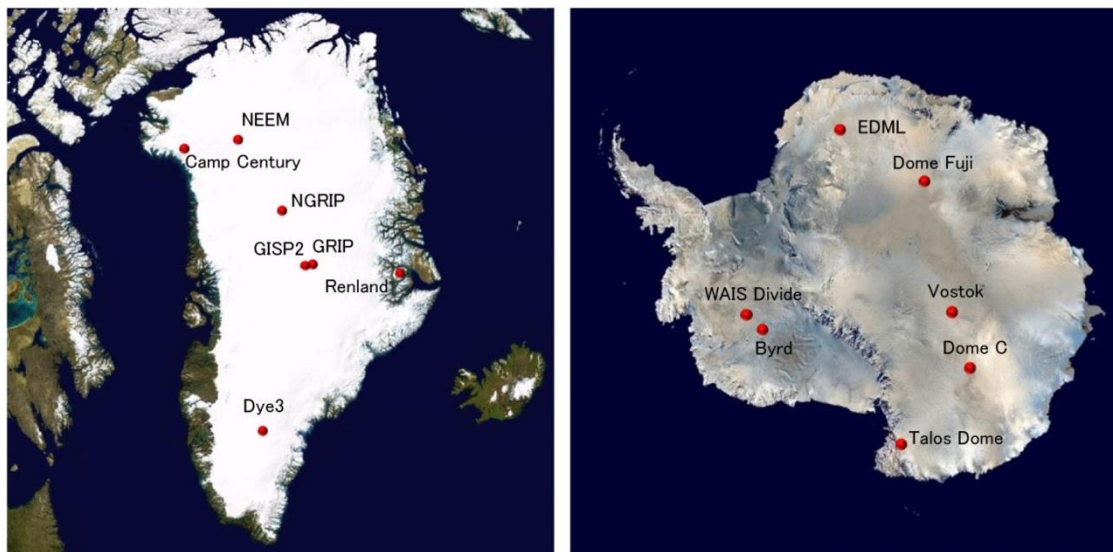


Figure 1 Map of the ice core sites in Greenland and Antarctica. This study uses ice cores from NEEM (Greenland), Dome Fuji (Antarctica), and Dome C (Antarctica). Image sources; NASA.

transition took place at the Mid-Brunhes Event 430 kyr BP, after which the amplitude of the 100 kyr climate oscillations increased, with substantially warmer interglacials, including periods warmer than at present [EPICA, 2004; Holden et al., 2011].

From the Greenland records, abrupt climate changes with millennial to centennial time scales have been found in the last glacial period [Dansgaard et al., 1993]. They are called Dansgaard-Oeschger events. In the Northern Hemisphere, they take the form of rapid warming episodes, typically over decades, followed by gradual cooling over a longer period. The effect appears to be less pronounced in the Southern Hemisphere [EPICA, 2006]. This linking has been explained by coupling mechanisms, including rapid bipolar ocean teleconnections and recently proposed bipolar atmospheric teleconnections (bipolar seesaw mechanism) [Broecker, 1998; Stocker and Johnsen, 2003; Pedro et al., 2011].

The last glacial termination, approximately 25.0–11.0 kyr BP, is the most recent climate transition, and thus crucial for understanding modern climate processes and evaluating climate models [Knorr and Lohmann, 2003; Lamy et al., 2007]. The process of the warming in Greenland and Antarctica over the last termination has been also explained by the bipolar seesaw mechanism, in which the temperatures of the two hemispheres oscillate via a coupling involving the Atlantic Meridional Overturning Circulation (AMOC) and atmospheric circulation [Anderson et al., 2009; Barker et al., 2009; Pedro et al., 2011].

The global ice sheets reached their maximum integrated volume around 20 kyr BP, which is defined as the Last Glacial Maximum (LGM) [Mix et al., 2001]. The last ice recession began in the Northern Hemisphere about 20 kyr BP [Denton et al., 2010], triggered by an increase in summer insolation [Abe-Ouchi et al., 2013]. The Laurentide ice sheet collapsed, and massive amounts of fresh water were injected to the Atlantic Ocean around 18 kyr BP, which weakened (or shut down) the AMOC [McManus et al., 2004; Denton et al., 2010]. A weakened AMOC cooled the northern hemisphere and warmed the southern hemisphere via oceanic and atmospheric teleconnections [Toggweiler et al., 2008; Barker et al., 2009]. In the southern hemisphere, westerlies and the Antarctic circumpolar current shifted southward [Toggweiler et al., 2008], which enhanced upwelling in the Southern Ocean and released CO₂ into the atmosphere [Anderson et al., 2009]. Around 14.7 kyr BP, the AMOC was restored, and the temperature increased to the interstadial climatic stage known as the Bølling-Allerød period in Greenland. Simultaneously, the Antarctic temperature decreased after 14.7 kyr BP in the Antarctic Cold Reversal (ACR). Around 13 kyr BP, massive amounts of fresh water were injected into the North Atlantic region, and the AMOC reduced again [McManus et al., 2004]. The

climate in Greenland returned to the near-glacial conditions of the Younger Dryas [Pedro et al., 2011]. On the other hand, upwelling in the Southern Ocean increased, accompanied by a rise in atmospheric CO₂ along with a rapid warming in sea-surface-temperature [Anderson et al., 2009; Denton et al., 2010], which lead to an increase in air temperature in Antarctica. Atmospheric CO₂ rose above a minimum level (about 260 ppmv) necessary to maintain warm conditions globally [Denton et al., 2010], so that, at around 11.7 kyr BP, both Greenland and Antarctica finally reached the Holocene climate stage.

1.3 Atmospheric aerosols

The ice cores provide records of past atmospheric aerosols in great temporal detail. Aerosols are colloid of fine solid particles or liquid droplets, in air or another gas [Hinds, 1999; Warneck, 1999]. They originate from wide variety of natural and anthropogenic sources. Primary aerosol particles are emitted directly as liquids or solids from land and/or sea surface. On the other hand, secondary aerosols are formed by gas to particle conversion and chemical reactions in the atmosphere [Hinds, 1999]. Such aerosols undergo various physical and chemical interactions and transformation, that is, changes of particle size, structure, and composition [Pöschl, 2005].

The natural soluble aerosols in the arctic region originate mainly from sea-salt (e.g., NaCl and MgCl₂) [e.g. Legrand and Delmas, 1988; Hansson., 1994; De Angelis et al., 1997; Legrand and Mayewski, 1997], terrestrial materials (e.g., CaSO₄ and CaCO₃) [e.g. Mayewski et al., 1994; Hansson., 1994; De Angelis et al., 1997; Legrand and Mayewski, 1997], bacterial decomposition in soils and biomass burning (e.g., NH₃, NH₄NO₃ and (NH₄)₂SO₄) [e.g., Fuhrer et al., 1996; Silvente and Legrand, 1993; Hansson and Holmén, 2001], smoke from biomass burning (e.g., KNO₃, K₂SO₄ and KCl) [e.g., Popovicheva, et al., 2014], marine biological activity and volcanism (H₂SO₄) [e.g. Legrand et al., 1988; Hansson and Saltzman, 1993; Legrand et al., 1997; Legrand and Mayewski, 1997], and the atmosphere, meaning both stratosphere and troposphere (HNO₃) [e.g Fuhrer and Legrand, 1997; Legrand and Mayewski, 1997; Röthlisberger et al., 2002].

The natural soluble aerosols in the Antarctic region are similar to those in the arctic region. However, Antarctica is far from the continents, so the contribution of aerosols originate from ocean is dominated but continental dust, biogenic activity and/or biomass burning is not much in the present [Legrand et al., 1997].

Atmospheric aerosols are one of the important drivers of climate change as well as greenhouse gases, especially considering shorter than glacial-interglacial time scale climate changes [e.g., IPCC, 2013]. Aerosols can provide feedbacks through two main effects. One is a direct effect in which aerosols scatter and absorb solar and infrared radiation [IPCC, 2001, 2007]. The other effect is an indirect effect in which aerosols change the microphysical and optical properties of cloud droplets acting as cloud condensation nuclei (CCN) [IPCC, 2001, 2007, 2013].

Atmospheric aerosol loading during glacial periods are generally much higher than those during interglacial periods [e.g., Petit et al., 1990; Lambert et al., 2012], the high concentrations of aerosol should have contributed the cooling at the glacial period [e.g., Yue, et al., 2011]. However, especially, an indirect effect has greater uncertainties. Thus, the estimation of a radiative forcing of aerosols has still large uncertainty [IPCC, 2013].

Sulfate aerosols are a key component of CCN in the atmosphere [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 sulfuric acid (H_2SO_4) 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 $1\text{ }\mu\text{m}$, much larger than the sub-micron diameters of H_2SO_4 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 .

1.4 Ion concentrations in inland Antarctica and Greenland

A useful technique for reconstructing past soluble aerosols from ice cores is the determination of dissolved ion species by chromatography [e.g. Legrand et al., 1993, 1997; Littot et al., 2002] or continuous flow analysis [Röthlisberger et al., 2000; Kaufmann et al., 2008; Bigler et al., 2011]. Representative ions in the Antarctic and Greenland ice cores are such as Na^+ , Mg^{2+} , Ca^{2+} , K^+ , NH_4^+ , H^+ , SO_4^{2-} , NO_3^- , Cl^- , and methanesulfonic acid. In general, Antarctica is surrounded by the Southern Ocean as reflected by much higher sea-salt contribution compare to continental aerosol. On the other hand, Greenland is surrounded by the continents as reflected by higher influence of continental aerosol.

Among many kinds of ion species, Ca^{2+} , Na^+ , SO_4^{2-} and NH_4^+ , which are major ions in the polar ice core, are focused on in this study.

1.4.1 Calcium ion (Ca^{2+})

The Ca^{2+} is a proxy for terrestrial materials (dust). The dust is mobilized by strong surface winds, uplifted and entrained into long-range transport in the westerly jet [Sun et al., 1998]. The Ca^{2+} is separated into a sea-salt (ss) and continental (non-sea-salt, shortened to nss) part, using sea-water and crustal ratios [Bigler et al., 2006].

In Antarctica, the Ca^{2+} concentration shows large variability between warm and cold periods. The high nss Ca^{2+} flux in the LGM decreased rapidly at the beginning of the last termination and reached low Holocene level before the ACR [e.g., Röthlisberger et al., 2003a; Fischer et al., 2007]. The difference of flux between the LGM and Holocene is about by a factor 15 (Table 1). The Ca^{2+} deposited during the glacial is derived mainly from Patagonia, Southern South America with substantial contributions also from Australia [Delmonte et al., 2004; Revel-Rolland et al., 2006; Fischer et al., 2007; Wolff et al., 2010].

In Greenland, the Ca^{2+} concentration also shows large variability between warm and cold periods. The flux in the LGM is higher than that in the Holocene by a factor 15–20 (Table 1). In the last termination, the Ca^{2+} concentration changed as a step. The high value in the LGM decreased dramatically (within 100 yr) at onset of the Bølling-Allerød, increased rapidly (100 ~ yr) at onset of the Younger Dryas, and then decreased dramatically again at onset of the Holocene [Steffensen et al., 2008]. The potential source for the Ca^{2+} in the LGM has been suggested as the east Asian desert [De Angelis et al., 1997; Fuhrer et al., 1999; Svensson et al., 2000; Ruth et al., 2007], whereas that in the Holocene has been suggested as the east Asian desert [Fuhrer et al., 1999; Svensson et al., 2000], North America [De Angelis et al., 1997], and Sahara desert [Mosher et al., 1993].

1.4.2 Sodium ion (Na^+)

The Na^+ is a proxy for sea-salt comes from open ocean [Mayewski et al., 1994; Fischer et al., 2007] and frost flower on the sea-ice [Rankin et al., 2002; Wolff et al., 2006; Röthlisberger et al., 2008]. Usually, the Na^+ is separated to ss Na^+ , using sea-water and crustal ratios [Bigler et al., 2006]. In Antarctica, the Na^+ shows lower amplitude compares to the Ca^{2+} , but the Na^+ concentration is much

higher in the cold periods than that in the warm periods [e.g., Röthlisberger et al., 2003a, 2003b; Wolff et al., 2010]. The difference of the flux between the LGM and the Holocene is about by a factor ~ 3 (Table 1). Most of the changes during the transition happened after the ACR [Röthlisberger et al., 2003b]. The ssNa^+ is used as a proxy for sea-ice extension in the Southern Ocean especially in the warm period when δD is above -420‰ [Röthlisberger et al., 2008].

In Greenland, the Na^+ concentration also shows lower amplitude compared to the Ca^{2+} , but the Na^+ concentration is also much higher in the cold periods than that in the warm periods [e.g., Mayewski et al., 1994; De Angelis et al., 1997]. Also, the Na^+ concentration changed as a step during the last termination. The difference of the flux between the LGM and the Holocene is about by a factor 3–4 (Table 1). Sea-salt aerosol formation is closely linked to cyclonic activity, providing high wind speeds on the ocean surface for efficient sea-salt aerosol formation [Fischer et al., 2007]. Pacific Ocean may be the primary source for sea-salt in glacial times [De Angelis et al., 1997; Fischer et al., 2001], and the northern Atlantic region may be the primary source for sea-salt in present [Fischer et al., 2007].

1.4.3 Sulfate ion (SO_4^{2-})

The SO_4^{2-} originates from various sources such as marine and terrestrial biosphere, volcanoes, and biomass burning, among which oceanic emissions, mainly in the form of dimethyl sulfide (DMS) dominates [Legrand et al., 1997].

In Antarctica, the SO_4^{2-} is used as a proxy for biogenic activity in the Southern Ocean. Wolff et al. [2010] showed that nssSO_4^{2-} flux remains constant within $\pm 15\%$ over the last 800 kyr and suggested that biogenic activity for the last 800 kyr does not have glacial-interglacial cycle.

In Greenland, discussion about SO_4^{2-} is much more complex than in Antarctica. Under the present climatic condition, contribution of anthropogenic emissions is high [Legrand et al., 1997]. The natural budget of SO_4^{2-} is dominated by eruptive as well as non-eruptive volcanic emissions and DMS emissions from marine biota in similar proportion [Legrand et al., 1997]. During the glacial period, SO_4^{2-} concentration is higher than in the Holocene. Legrand et al. [1997] suggested that increase of SO_4^{2-} in the glacial ice reflects enhanced terrestrial input (gypsum and sulfatized CaCO_3).

1.4.4 Ammonium ion (NH_4^+)

The NH_4^+ is originated from NH_3 emission, which have predominantly continental source of biogenic origin [Fuhrer et al., 1993]. In Antarctica, the NH_4^+ is a minor contribution because Antarctica is far from continents where main source of NH_4^+ is located [Legrand et al., 1997]. On the other hand, Greenland is surrounded by continents, so the mean level of NH_4^+ is high in the present [Legrand et al., 1997]. The NH_4^+ concentration in Greenland increased along with retreating the Laurentide ice sheet and spreading vegetation-covered area in North America where major source of NH_4^+ to Greenland is located [Fuhrer et al., 1996; Mayewski et al., 1995]. The NH_4^+ concentration in starts to increase slightly before 16 kyr BP from very low values in in the last glacial period, and became one of the dominant cation in the Holocene [Hansson, 1994; Fuhrer and Legrand, 1997; Fuhrer et al., 1996; Hansson and Holmén, 2001].

Table 1 Ratios of observed ion concentrations in the Dome Fuji, Dome C and NEEM ice cores between the LGM and the Holocene. Dome Fuji profile is derived from Oyabu et al. [2014], the Dome C profile is derived from Wolff et al. [2006] and the NEEM profile is derived from Mayewski et al. [1997].

LGM/Holocene	Ca^{2+} flux	Na^+ flux	SO_4^{2-} flux	NH_4^+ flux
DF	11	2.5	1	–
DC	15	3	1.2	–
GISP2	15-20	3-4	1.5-2.5	8

1.5 Deducing salts compositions and individual particle analysis

Many kinds of aerosols such as described in section 1.3 should be preserved as soluble salt particles in the Greenland and Antarctic ice cores. To better understand past atmospheric environment, reconstruction of chemical compositions of the soluble salt particles is required. However, it was difficult to analyse salts compositions directly.

Several studies have deduced the salt compositions from the measured ion concentrations. For Antarctica, Legrand et al. [1988] calculated the sea-salt and terrestrial-salt concentrations of the Vostok ice by using sea-water composition. They argued that the Holocene soluble impurities were mainly H_2SO_4 , HNO_3 , HCl , NaCl , and Na_2SO_4 . For the LGM, the ice instead contained primarily H_2SO_4 , NaCl , and CaSO_4 . 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. [2003b], 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 Na_2SO_4 prior to NaCl , and Ca^{2+} forms sulfate prior to nitrate. For the LGM, they deduced that there were CaSO_4 , Na_2SO_4 , NaCl and negligible H_2SO_4 , whereas the Holocene had Na_2SO_4 , H_2SO_4 , little CaSO_4 and negligible NaCl . For Greenland, Mayewski et al. [1994] and De Angelis et al. [1997] has been suggested that the more than 50% of Ca^{2+} was deposited as CaCO_3 without being neutralization by the acids in the atmosphere, due to high cation contributions under the glacial conditions. Iizuka et al. [2008] estimated that the major components of soluble salts in the LGM are NaCl , CaSO_4 , and CaCO_3 .

Studies on the direct measurement of the chemical compositions of soluble particles in the Antarctic ice core have been more advanced than those in the Greenland ice cores. Earlier studies used the 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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Later, Ohno et al. [2006] showed that the primary soluble impurities are $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ for the glacial maxima and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ 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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and the sulfate-salt compositions from LGM to Holocene can be explained by ion balance arguments.

Iizuka et al. [2009] developed the ice sublimation 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 Na_2SO_4 . With the same method, Iizuka et al. [2012b] showed a time-series dataset of soluble salts (CaSO_4 , Na_2SO_4 , 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 , Na_2SO_4 , and H_2SO_4) flux (consistent with findings at Dome C [Wolff et al., 2010]), the sulfate-salt (CaSO_4 and Na_2SO_4) 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.

On the other hand, in the Greenland ice core study, only one study has been reported the chemical compositions of soluble particles in the ice core. Sakurai et al. [2009] analysed particles in the GRIP ice, and found that CaCO_3 was contained in the glacial ice.

1.6 Objective of this study

The objective of this study is to clarify the temporal variations in the chemical compositions of past soluble aerosols in Greenland and Antarctic ice cores, and the interaction between past atmospheric aerosols (sulfate-salt aerosols) and climate changes during the last termination, the most recent climatic transition. This objective is achieved by analysis of the chemical compositions of solid particles preserved in the Greenland and Antarctic ice cores.

For the Antarctic ice core (Dome Fuji), the temporal variations in the chemical compositions of soluble salt particles have been cleared on the glacial-interglacial time scale. However, millennial to centennial time scale data, which can reveal detailed variations during the last termination, do not exist. Also, there is almost no study on the soluble salt particles in Antarctic ice cores other than the Dome Fuji ice core. In this study, I measured chemical compositions of solid particles preserved in the Dome Fuji and Dome C ice cores on a time scale of several hundred years.

For Greenland, little is known about the chemical compositions of soluble salt particles. In this study, I measured chemical compositions of solid particles preserved in the NEEM ice core over the last glacial-interglacial cycle. Especially, an analysis with a resolution of several hundred years was carried out during the last termination, and compared to Antarctica.

CHAPTER 2

2 Methods

This study was mainly performed by the analyses on chemical components of soluble salt particles using the ice-sublimation method, which can extract soluble salt particles without melting. This chapter explains the procedures of the ice-sublimation method and analysis method, and used data sets. The analyses were performed on the Dome Fuji ice core drilled in the East Antarctic ice sheet (77.2°S, 39.4°E; 3810 m a.s.l), the Dome C ice core drilled in the East Antarctic ice sheet (75°06'S, 123°21'E; 3233 m a.s.l), and the NEEM ice core drilled in the Northwest Greenland ice sheet (77.45°N, 51.06°W; 2450 m a.s.l). Detailed description about each ice cores are described in Chapter 1.

2.1 Ice sublimation method

2.1.1 Ice core samples

2.1.1.1 Dome Fuji ice core

The ice core was stored in a cold room at -50°C at the Institute of Low Temperature Science (ILTS), Hokkaido University (Japan), below the eutectic temperatures of all major salts. The sample depths used here are from 294.96 (Early Holocene: 9.6 kyr BP) to 579.80 m (LGM: 25.0 kyr BP) (Figure 2.1, Table 2.1). 47 core sections were selected. Each section is a $100\times 30\times 5\text{ mm}^3$ cuboid. The length of each cuboid sample represents 5–10 years. The average time resolution is about 350 years.

2.1.1.2 Dome C ice core

The ice cores were transported in the frozen state from the Laboratoire de Glaciologie et Géophysique de l'Environnement (France) cold storage facility to a cold laboratory at the Department of Physical Geography and Quaternary Geology, Stockholm University (Sweden). There, they were

preserved at temperatures of -25°C . The sample depths used here are from 222.75 (Middle Holocene: 6.8 kyr BP) to 570.50 m (LGM: 26.0 kyr BP) (Figure 2.1, Table 2.2). 30 core sections were selected. Each section is a $100\times 40\times 30\text{ mm}^3$ cuboid. The length of each cuboid sample represents 5–10 years. The average time resolution is about 640 years.

2.1.1.3 NEEM core

The ice core samples applied in this study were transported from the field to the Niels Bohr Institute (Denmark) cold storage facility to a cold laboratory at the Department of Physical Geography and Quaternary Geology, Stockholm University (Sweden), where they were preserved at temperatures of -25°C .

Stratigraphic disruptions are identified in the NEEM ice core below 2209.60 m depth [NEEM community members, 2013], and for this study samples have been selected from the section above 2200 m. The applied NEEM ice core time scale is from Rasmussen et al. [2013]. 93 sections from 7 climatic stages were selected by referring to the NEEM water isotope profile (unpublished). The event stratigraphies divide the characteristic sequence of Greenland climate changes in the glacial periods into numbered Greenland Interstadials (GI) and Greenland Stadials (GS) as following Rasmussen et al. [2014]. 26 sections from the Holocene (0.9–11.7 kyr BP), 3 sections from Younger Dryas (YD; GS-1, 12.0–12.6 kyr BP), 7 sections from Bølling Allerød (BA; GI-1, 12.9–14.6 kyr BP), 20 sections from LGM (GS-2 and GS-3, 15.0–26.9 kyr BP), 17 sections from warm stages of Dansgaard-Oeschger (DO) event (DO-w; GI-3–24), 13 sections from cold stages of DO event (DO-c; GS-4–22), and 7 sections from stratigraphic disruptions section (SDS) (118 kyr BP–Before Eemian) (Figure 2.1, Table 2.3). Each section is a $550\times 70\times 10\text{ mm}^3$ cuboid. The average time resolution during the last termination is about 280 years.

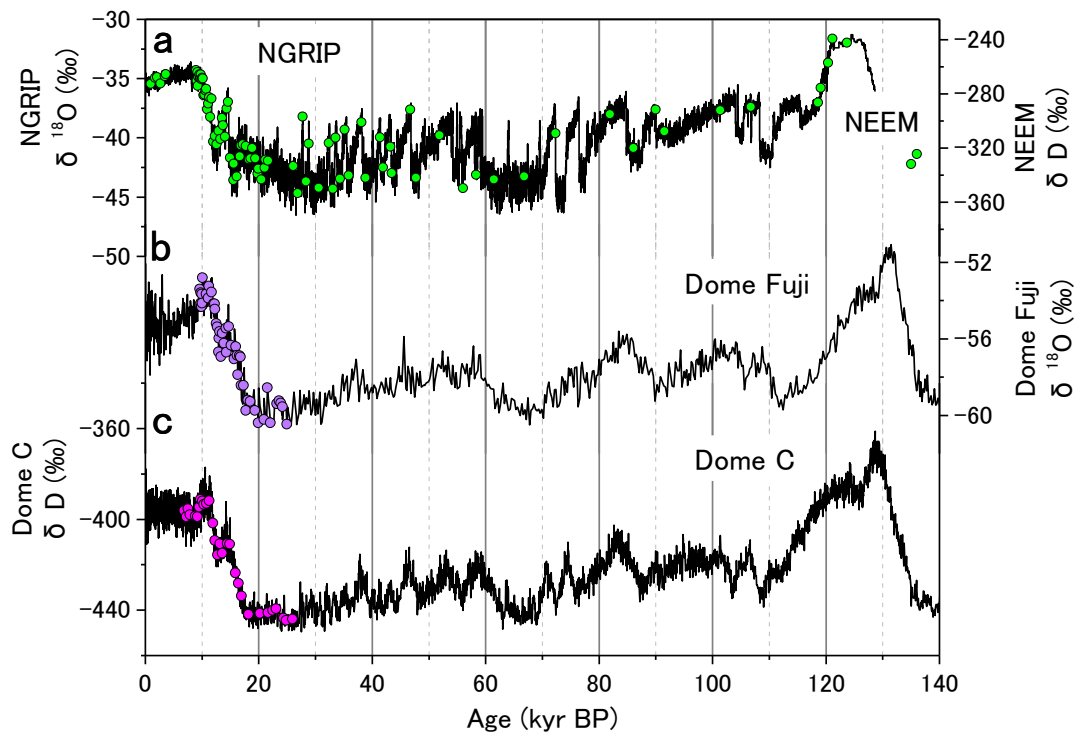


Figure 2.1 Water isotope of the last glacial-interglacial cycle and analyzed samples. (a) 0–119.1 kyr BP; $\delta^{18}\text{O}$ of the NGRIP ice core [Rasmussen et al., 2014 and their references]. 119.1 kyr BP~; δD profile of the NEEM ice core [NEEM community members, 2013]. (b) $\delta^{18}\text{O}$ profile of the Dome Fuji ice core [Watanabe et al., 2003a]. (c) δD profile of the Dome C ice core [Jouzel et al., 2007]. Green, purple and pink dots on the each curve indicates measured samples in this study.

Table 2.1 Overview of the Dome Fuji ice core sections used for this study

Depth (m)	Age (kyr BP)	Number of particles	Average diameter
294.96	9.6	234	3.39
299.15	9.8	215	3.32
300.15	9.8	226	3.57
302.40	9.9	215	3.13
304.15	9.9	212	3.39
306.15	10.0	233	3.31
307.90	10.1	226	3.45
326.40	10.7	219	1.90
339.38	11.1	212	1.97
340.38	11.2	235	2.35
352.92	11.7	230	2.25
362.44	12.0	365	2.00
366.44	12.2	229	3.19
368.44	12.3	211	2.29
373.94	12.5	215	3.02
378.90	12.7	198	1.59
382.86	12.9	223	3.44
384.36	13.0	224	2.07
388.31	13.1	220	3.44
393.31	13.3	228	2.60
398.84	13.5	230	2.74
406.09	13.9	235	3.28
413.86	14.2	204	2.01
414.36	14.3	230	2.07
423.35	14.7	227	3.15
431.85	15.1	232	2.99
443.35	15.6	406	2.65
448.85	16.0	228	2.17
453.85	16.2	223	3.41
455.85	16.3	235	3.09
460.85	16.6	223	3.44
463.85	16.8	425	2.06
465.85	16.9	438	2.64
473.35	17.3	237	1.86
479.35	17.7	246	2.50
484.35	18.1	237	2.10
490.35	18.5	208	3.51
502.35	19.3	274	2.14
510.33	19.9	248	2.92
524.25	20.9	243	2.21
532.75	21.5	242	3.23
540.25	22.0	233	2.41
554.96	23.2	237	2.35
561.00	23.6	229	2.82
565.36	23.9	230	2.87
569.25	24.2	233	1.92
579.80	24.9	231	3.33

Table 2.2 Overview of the Dome C ice core sections used for this study

Depth (m)	Age (kyr BP)	Number of particles	Average diameter
222.75	6.80	205	2.13
233.75	7.21	212	2.00
241.45	7.50	207	2.59
251.35	7.85	201	2.35
276.65	8.81	197	2.49
287.10	9.19	200	2.38
296.45	9.50	206	2.32
305.25	9.72	206	3.09
313.50	10.06	210	2.45
321.75	10.33	204	2.56
334.95	10.77	202	1.91
350.35	11.28	202	2.34
368.50	11.91	202	2.44
377.30	12.27	207	2.02
386.65	12.73	194	2.33
395.45	13.17	205	2.05
403.15	13.55	201	2.61
422.95	14.47	202	2.38
430.65	14.85	202	1.98
449.35	15.86	210	1.98
458.15	16.40	199	2.53
465.85	16.95	206	2.18
481.25	18.17	204	2.56
505.45	20.21	202	2.18
521.95	21.63	205	2.13
531.85	22.48	207	2.50
538.45	23.06	203	2.45
553.30	24.36	204	1.89
558.25	24.82	202	2.60
570.35	25.95	201	1.80

Table 2.3 Overview of the NEEM ice core sections used for this study. The event stratigraphies divide the characteristic sequence of Greenland climate changes in the glacial period into numbered Greenland Interstadials (GI) and Greenland Stadials (GS) as following Rasmussen et al. [2014].

	Depth (m)	Age (kyr BP)	Number of particles	Climate stage	Average diameter		Depth (m)	Age (kyr BP)	Number of particles	Climate stage	Average diameter
Holocene	219.45	0.9	574		1.05	DO-w	1640.10	27.7	531	GI-3	1.99
	376.75	1.7	669		2.23	DO-c	1646.70	28.3	528	GS-4	1.38
	441.65	2.1	585		2.40	DO-w	1652.20	28.8	515	GI-4	1.26
	544.50	2.7	518		2.51	DO-c	1669.25	30.6	529	GS-5.1	1.46
	665.50	3.4	476		1.60	DO-w	1687.40	32.3	511	GI-5.2	1.19
	689.15	3.6	662		2.25	DO-c	1695.10	33.1	301	GS-6	2.23
	1282.05	8.9	309		2.11	DO-w	1700.60	33.6	303	GI-6	1.86
	1289.20	9.0	301		2.40	DO-c	1708.30	34.3	221	GS-7	2.04
	1296.35	9.2	300		2.22	DO-w	1718.20	35.2	310	GI-7	2.11
	1302.95	9.3	307		1.96	DO-c	1727.00	35.9	306	GS-8	1.98
	1310.65	9.4	304		3.22	DO-w	1757.25	38.1	307	GI-8	2.04
	1318.90	9.5	299		2.33	DO-c	1765.50	38.8	307	GS-9	2.19
	1326.05	9.6	306		2.43	DO-w	1790.25	41.4	305	GI-10	1.88
	1332.65	9.8	315		1.82	DO-c	1795.75	41.9	303	GS-11	2.34
	1339.80	9.9	293		1.91	DO-w	1808.95	43.2	306	GI-11	2.12
	1346.40	10.0	305		2.64	DO-c	1811.70	43.5	303	GS-12	2.12
	1353.55	10.2	306		2.73	DO-w	1844.70	46.7	282	GI-12	2.11
	1359.60	10.3	312		1.92	DO-c	1852.95	47.7	300	GS-13	1.97
	1367.30	10.4	271		3.16	DO-w	1888.70	51.9	741	GI-14	1.73
	1373.90	10.6	307		1.82	DO-c	1925.00	56.0	536	GS-16.1	1.44
	1381.60	10.8	301		2.83	DO-w	1942.60	58.3	615	GI-16.2	1.64
	1388.20	10.9	313		2.50	DO-c	1963.50	61.5	528	GS-18	1.63
	1395.35	11.1	307		2.00	DO-c	1986.60	66.8	515	GS-19.1	1.45
	1401.95	11.3	313		2.26	DO-w	2010.25	72.3	307	GI-19.2	2.02
	1409.10	11.5	298		1.99	DO-w	2063.60	81.9	304	GI-21.1	2.22
	1416.80	11.7	306		2.27	DO-c	2096.60	86.0	309	GS-22	2.13
YD	1423.95	12.0	305	GS-1	2.00	DO-w	2128.50	90.0	304	GI-22	2.06
	1430.55	12.3	307	GS-1	2.06	DO-w	2137.85	91.5	303	GI-23.1	2.16
	1437.15	12.6	309	GS-1	2.07	DO-w	2180.20	101.4	308	GI-23.1	2.22
BA	1444.30	12.9	301	GI-1	2.24	DO-w	2195.60	106.7	308	GI-24.1	1.98
	1451.45	13.2	333	GI-1	3.14		2213.20	118.6	300	GS-26	0.99
	1458.60	13.5	306	GI-1	2.20		2285.80	119.1	301	GS-26	2.68
	1464.10	13.7	309	GI-1	2.25		4209.00	120.4	302	Eemian	2.52
	1472.35	14.1	305	GI-1	1.95		4345.00	121.2	537	Eemian	1.16
	1478.95	14.3	268	GI-1	2.73	SDS	4367.00	123.7	534	Eemian	1.23
	1486.10	14.6	329	GI-1	2.42		4485.00		534	Before Eemian	1.23
LGM	1492.70	15.0	306	GS-2	1.93		4495.00		420	Before Eemian	2.21
	1499.85	15.5	272	GS-2	3.02						
	1501.50	15.6	515	GS-2	1.33						
	1507.55	16.1	301	GS-2	2.06						
	1514.70	16.7	300	GS-2	1.87						
	1517.45	16.8	738	GS-2	1.64						
	1521.85	17.2	305	GS-2	2.29						
	1528.45	17.7	312	GS-2	1.82						
	1535.60	18.2	308	GS-2	2.94						
	1540.00	18.5	732	GS-2	1.95						
	1543.30	18.8	307	GS-2	2.59						
	1550.45	19.4	304	GS-2	2.35						
	1556.50	19.8	539	GS-2	2.39						
	1557.60	19.9	309	GS-2	2.01						
	1564.20	20.5	301	GS-2	2.98						
	1571.35	21.0	306	GS-2	1.87						
	1573.00	21.1	735	GS-2	1.66						
	1577.95	21.6	304	GS-2	2.47						
	1622.50	26.1	737	GS-3	1.79						
	1630.20	26.9	763	GS-3	2.15						

2.1.2 Extracting non-volatile particles by ice sublimation system

To analyse the embedded impurities, I followed the sublimation-EDS method [Iizuka et al., 2009] (Figure 2.2). The sublimation systems which are systems for extracting non-volatile particles without melting ice were set up at ILTS and Stockholm University. Sample surfaces were decontaminated on a clean bench in the cold room using a ceramic knife. About 1 g of decontaminated sample was pulverized using a clean ceramic knife and placed on a polycarbonate membrane filter with pores 0.45 μm in diameter, which was set in a sublimation chamber. This sublimation chamber was set in a freezer where clean, dry air (compression air pressure of 0.55 MPa, dew point of $-65\text{ }^{\circ}\text{C}$) flowed through at a rate of 15 L min^{-1} . The non-volatile particles of Dome Fuji were extracted with $-50\text{ }^{\circ}\text{C}$ for 100 hours at ILTS, those of Dome C were extracted with $-50\text{ }^{\circ}\text{C}$ for 100 hours at Stockholm University, and those of NEEM were extracted with $-40\text{ }^{\circ}\text{C}$ for 50 hours at Stockholm University.

After sublimation, each filter yielded several hundreds of non-volatile particles exceeding 0.45- μm diameter. Their constituent elements and diameter were measured using a JSM-6360LV (JEOL) SEM (scanning electron microscope) and a JED2201 (JEOL) EDS (energy dispersive X-ray spectroscopy) system at ILTS. To avoid electrical charging of the filter and to improve analysis accuracy, the filter was coated with a Pt film by 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 seconds. To be counted as a non-volatile 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 (%). Also, the C, Cr, Fe, and Pt were observed, but interpret 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.

In order to check if there is any contamination during the sublimation process, the sublimation system was tested 2 times without setting the ice sample on the filter in the sublimation chamber. After flowing air for 100 hours, the filter was observed by SEM-EDS. As a result, only 3 to 5 of particles with C and O were found. The system obtains more than 700 particles from 1 g ice, so the contamination test shows the contribution of particles from the sublimation system is less than 1 %. Since particles containing only C and O are not counted as non-volatile particles in this study, I conclude that results of this study are not affected by the contamination from sublimation system.

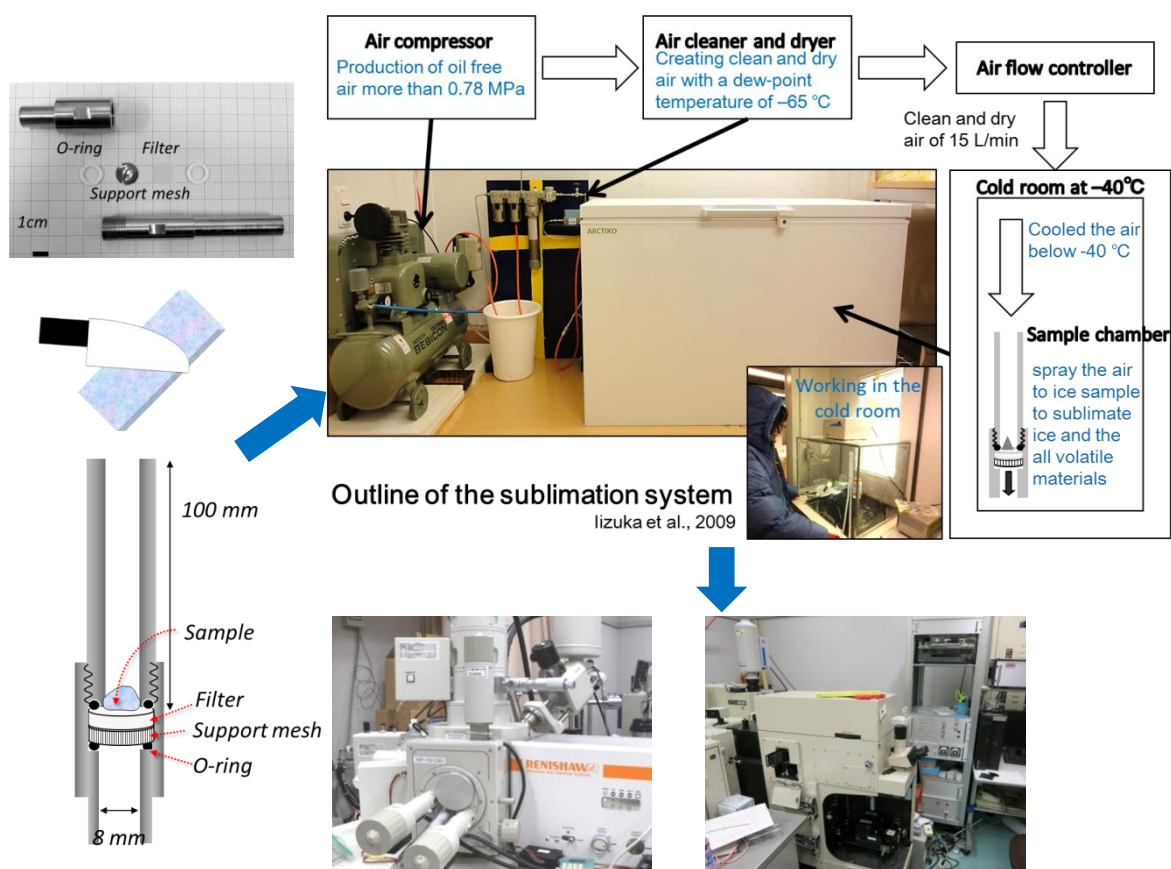


Figure 2.2 Outline of the sublimation system

2.1.3 Chemical compositions of single particles from their elemental distribution

From elemental compositions of particles detected by EDS measurement, chemical compositions of single particles were determined (detailed are discussed in section 3.2). The non-volatile particles are classified into insoluble dust, soluble sulfate salts, soluble chloride salts, and others as follows. If a particle contains Si, the particle is regarded as insoluble dust (silicate); if the particle has S, the particle is assumed to have a sulfate salt; and if it has Cl, the particle is assumed to have chloride salts. More specifically, a particle containing Ca and S is assumed to have CaSO_4 , whereas that with Na and S has Na_2SO_4 . A particle containing Mg and S is assumed to have MgSO_4 , that with K and S has K_2SO_4 , and any other sulfate-salt particle is labeled “other-S”. A particle containing Na and Cl is assumed to have NaCl, Ca and Cl is assumed to have CaCl_2 , and any other chloride-salt particle is labeled “other-Cl”. A particle containing Ca without S and Cl is assumed labeled as “other-Ca”, and a particle containing Na without Si, S and Cl is labeled as “other-Na”.

The molar mass of CaSO_4 , CaCl_2 , other-Ca, Na_2SO_4 , NaCl, and other-Na for each sample of Dome Fuji and Dome C ice cores, and CaSO_4 , CaCl_2 , other-Ca, Na_2SO_4 , NaCl, other-Na, MgSO_4 , K_2SO_4 , and other-S of NEEM ice core are calculated using the spectrum ratios of each element. The calculation procedure for the molar masses are based on the previous studies [Iizuka et al. 2012a, 2012b], but I arranged to suit for this study. The moles of Na, Mg, Ca, K, S, and Cl are calculated 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 is estimated as

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

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

where CA and R are the cross-sectional area and inferred radius, respectively. The particle mass m is

$$m = \rho V$$

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

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

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 nine major detected elements: O, Si, Al, S, Cl, Na, Mg, Ca and K. I assume that all particles consist almost entirely of these nine elements, so that $\sum A_i = 1$. From above calculation, $[\text{Ca}]$, $[\text{Na}]$, $[\text{Mg}]$, $[\text{K}]$, $[\text{S}]$ and $[\text{Cl}]$ (eq) were derived. Using these moles of each elements, masses of salts are derived following equations.

When a particle has Na and S, the molar mass of Na_2SO_4 is equal to the smaller mass of either Na or S. If $[\text{Na}] < [\text{S}]$, then $[\text{Na}_2\text{SO}_4] = [\text{Na}]$ (eq). If $[\text{Na}] > [\text{S}]$, then $[\text{Na}_2\text{SO}_4] = [\text{S}]$ (eq). The same procedure applies to $[\text{CaSO}_4]$ and $[\text{NaCl}]$. When a particle has more than one cations (Na, Mg, Ca, and/or K) and/or anions (S and/or Cl), the molar ratio of salts depends on that of each element as follows.

If $[\text{Ca}] + [\text{Na}] + [\text{Mg}] + [\text{K}] > [\text{S}] + [\text{Cl}]$ (eq),

$$[\text{CaSO}_4] = \frac{[\text{Ca}]}{([\text{Ca}] + [\text{Na}] + [\text{Mg}] + [\text{K}])} \times [\text{S}] ,$$

$$[\text{Na}_2\text{SO}_4] = \frac{[\text{Na}]}{([\text{Ca}] + [\text{Na}] + [\text{Mg}] + [\text{K}])} \times [\text{S}] .$$

$$[\text{MgSO}_4] = \frac{[\text{Mg}]}{([\text{Ca}] + [\text{Na}] + [\text{Mg}] + [\text{K}])} \times [\text{S}] .$$

$$[\text{K}_2\text{SO}_4] = \frac{[\text{K}]}{([\text{Ca}] + [\text{Na}] + [\text{Mg}] + [\text{K}])} \times [\text{S}] .$$

$$[\text{other-S}] = 0$$

$$[\text{CaCl}_2] = \frac{[\text{Ca}]}{([\text{Ca}] + [\text{Na}] + [\text{Mg}] + [\text{K}])} \times [\text{Cl}]$$

$$[\text{NaCl}] = \frac{[\text{Na}]}{([\text{Ca}] + [\text{Na}] + [\text{Mg}] + [\text{K}])} \times [\text{Cl}]$$

$$[\text{other-Ca}] = 0$$

$$[\text{other-Na}] = 0.$$

If $[\text{Ca}] + [\text{Na}] + [\text{Mg}] + [\text{K}] < [\text{S}] + [\text{Cl}]$ (eq),

$$[\text{CaSO}_4] = [\text{Ca}] \times \frac{[\text{S}]}{[\text{S}] + [\text{Cl}]},$$

$$[\text{Na}_2\text{SO}_4] = [\text{Na}] \times \frac{[\text{S}]}{[\text{S}] + [\text{Cl}]},$$

$$[\text{MgSO}_4] = [\text{Mg}] \times \frac{[\text{S}]}{[\text{S}] + [\text{Cl}]} ,$$

$$[\text{K}_2\text{SO}_4] = [\text{K}] \times \frac{[\text{S}]}{[\text{S}] + [\text{Cl}]} ,$$

$$[\text{other-S}] = [\text{S}] - [\text{CaSO}_4] - [\text{Na}_2\text{SO}_4] - [\text{MgSO}_4] - [\text{K}_2\text{SO}_4] .$$

$$[\text{CaCl}_2] = [\text{Ca}] \times \frac{[\text{Cl}]}{[\text{S}] + [\text{Cl}]} ,$$

$$[\text{NaCl}] = [\text{Na}] \times \frac{[\text{Cl}]}{[\text{S}] + [\text{Cl}]} ,$$

$$[\text{other-Ca}] = [\text{Ca}] - [\text{CaSO}_4] - [\text{CaCl}_2]$$

$$[\text{other-Na}] = [\text{Na}] - [\text{Na}_2\text{SO}_4] - [\text{NaCl}] .$$

If a particle does not have S and Cl,

$$[\text{Na}_2\text{SO}_4] = 0$$

$$[\text{CaSO}_4] = 0$$

$$[\text{MgSO}_4] = 0$$

$$[\text{K}_2\text{SO}_4] = 0$$

$$[\text{other-S}] = 0$$

$$[\text{CaCl}_2] = 0$$

$$[\text{NaCl}] = 0$$

$$[\text{other-Ca}] = [\text{Ca}]$$

$$[\text{other-Na}] = [\text{Na}] \text{ (if Na-particle contains Si, } [\text{Na}] = 0)$$

Uncertainty in the molar masses was calculated as follows. A particle was selected at random. If, for example, it contained Na and S, then I repeatedly (20x) measured its atomic ratios of Na. Then the ratio of standard deviations to average values of the 20 measurements (the coefficient of variation; CV_{Na}) was calculated. In the same way, coefficients of variation of six elements (Na, Mg, Ca, K, S and Cl) were obtained. The coefficients of variation of six elements were similar to each other, so I picked average value ($\text{CV} = 0.22$).

For calculating the molar masses of non-volatile particles, I 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, then measuring the deviation between their actual shadow area and comparing to the idealized ellipse shadow area. As a result, 95% of the particles had areas that differed by less than 20%. From this result, I calculated the error in particle volume. The total uncertainty for the moles of salts is 33.5–51.0 %.

2.2 High-resolution analysis on NEEM ice core

High-resolution analysis was performed on selected sections of the NEEM ice cores. Ice core samples were selected from 1302.95–1303.50 m (Holocene; 9.3 kyr BP), and 1555.95–1556.50 m (LGM; 19.8 kyr BP) (Table 2.4). The layers which focusing on were determined by high resolution data set of dust, Ca^{2+} , Na^+ , NO_3^- , and NH_4^+ concentrations analysed by Continuous Flow Analysis (CFA) system at the University of Bern. For the Holocene ice, clear layers and cloudy bands are not as prominent due to the much lower impurity content. However, ion and dust concentrations show clear seasonal variability [Rasmussen et al., 2006], so the seasonality can be determined from their concentrations. Based on the CFA records, 4 layers of 1 cm thickness were selected from the Holocene section: Holocene-01 (1303.18m; Na^+ peak), Holocene-02 (1303.24m; NH_4^+ and NO_3^- peak), Holocene-03 (1303.30m; dust and Ca^{2+} peak), and Holocene-04 (1303.35m; NH_4^+ and NO_3^- peak). From visual observation, 5 layers were selected from the LGM section. LGM-01, LGM-03, and LGM-05 are from clear layers (1560.00, 1556.17, and 1556.25 m), and LGM-02 and LGM-04 (1556.13 and 1556.22 m) are from cloudy bands with high dust and Ca^{2+} concentrations

The ice samples were cut by hand saw and shaved by a ceramic knife for decontamination of the target layer. Then several mm of the target layer were placed in the sublimation chamber as and analysed as described in section 2.1. Some 200–500 particles were analysed for each sample.

Table 2.4 Sample list of the high resolution analysis on NEEM ice

		Depth (m)	Age (kyr BP)	Number of particles	Average diameter
Holocene-01	Na^+ peak	1303.18	9.3	206	2.33
Holocene-02	NO_3^- & NH_4^+ peak	1303.24		202	2.69
Holocene-03	Dust & Ca^{2+} peak	1303.30		200	2.70
Holocene-04	NO_3^- & NH_4^+ peak	1303.35		198	2.83
LGM-01	clear layer	1556.00	19.8	208	2.19
LGM-02	cloudy band	1556.13		524	1.24
LGM-03	clear layer	1556.17		510	1.07
LGM-04	cloudy band	1556.22		511	1.11
LGM-05	clear layer	1556.25		514	1.02

2.3 Water immersion experiments

The water immersion experiments has done on the Holocene (2.7 kyr BP) and LGM (19.8 kyr BP) sections of NEEM ice core (Table 2.5) as following Iizuka et al. [2009] and Iizuka et al., [2012a]. After extracting the non-volatile particles, their elemental compositions were measured by SEM-EDS without Pt coating. Then the water-soluble particles were dissolved by immersing the filter in ultra-pure water at 25 °C for 24 hours. After drying, the filter was coated by a Pt film and the residue of insoluble particles remaining on the filter was analysed once more using SEM-EDS. In this way, the elemental compositions of non-volatile and insoluble particles from the same sample were measured. From the Holocene section, 518 non-volatile particles and 218 insoluble particles were analyzed. From the LGM section, data from 539 non-volatile particles and 232 insoluble particles were collected. After considering the possible remaining combination of elements, I made a classification of non-volatile particles into insoluble and soluble particles.

Table 2.5 Sample list of the water immersion experiments on the NEEM ice core

	Depth (m)	Age (kyr BP)	Number of particles	Average diameter
Holocene_non-volatile	543.95	2.7	518	2.51
Holocene_water			218	1.16
LGM_non-volatile	1555.95	19.8	539	2.39
LGM_water			232	1.3

2.4 Raman-EDS Analysis

Previous study predicted that CaCO_3 and $\text{Ca}(\text{NO}_3)_2$ are preserved in Greenland ice cores [Mayewski et al., 1994; De Angelis et al., 1997; Iizuka et al., 2008]. However, the SEM-EDS analysis cannot determine CaCO_3 and $\text{Ca}(\text{NO}_3)_2$, so the micro-Raman spectroscopy was used to identify CaCO_3 and $\text{Ca}(\text{NO}_3)_2$.

Glacial ice from 19.8 kyr BP and 28.4 kyr BP were selected. (Table 2.6). A certain amount of soluble Ca containing particles was observed during the SEM-EDS measurement. To determine the compositions of such soluble Ca containing particles, the non-volatile particles were measured by the micro-Raman spectroscopy. Glacial ice from 19.8 kyr BP and 28.3 kyr BP were selected. A $5 \times 5 \times 1 \text{ mm}^3$ Cr plate was mounted to a membrane filter before placing the ice sample in the sublimation chamber. Then about 1 g of ice sample was placed on the Cr plate, and volatile materials were sublimated at -40°C as described in section 2.1 at Stockholm University. Extracted particles were measured at random by micro-Raman spectroscopy at ILTS (Japan). The Micro-Raman spectrometer has a triple monochromator (Jobin-Yvon, T64000) equipped with a charge-coupled device (CCD) detector (Jobin-Yvon, Spectraview-2D). Laser light of wavelength 514.5 nm and power 150 mW was focused to a particle for 60 sec. To identify the chemical compositions of particles, the observed spectra were compared with those of the reference specimens: CaCO_3 (Kishida Chemical Co., Ltd.), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd.) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Kishida Chemical Co., Ltd.) For the dolomite ($\text{CaMg}(\text{CO}_3)_2$), I referred to spectra from the open database [Downs, 2006]. After the micro-Raman analysis, the elemental compositions of non-volatile particles of the same plates were measured by SEM-EDS. Almost all particles on the Ca plate were also measured by SEM-EDS, thus, the result of Raman and that of SEM-EDS can be compared by 1:1.

Table 2.6 Sample list of the Raman-EDS analysis

Depth (m)	Age (kyr BP)	Number of particles	Average diameter
1555.95	19.8	223	3.12
		208	
		200	
1630.20	28.3	206	3.15

2.5 Ion concentrations

The Dome Fuji ion concentrations (Ca^{2+} , Na^+ , SO_4^{2-} , Cl^- , and NO_3^-) of 122 samples from 326.4 m to 579.8 m were analysed by an ion chromatography (Dionex DX-500) at the National Institute of Polar Research. I added them to the existing dataset of 172 samples of Watanabe et al. [2003b] to make 294 samples. In the SO_4^{2-} data, 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 σ are calculated using non-sea-salt SO_4^{2-} values, yielding $M = 137.6$ ppb and $\sigma = 64.6$ ppb. I select eight spikes with values exceeding $M + 2\sigma = 266.7$ ppb. The nssSO_4^{2-} calculation followed the method in Bigler et al. [2006].

The Dome C ion concentrations (Ca^{2+} , Na^+ , SO_4^{2-} , Cl^- , and NO_3^-) of 161 data from 221.1 m to 564.3 m were obtained from published data. The Ca^{2+} , Na^+ , and SO_4^{2-} concentrations were derived from Wolff et al. [2006], Cl^- concentration was derived from Röthlisberger et al. [2003b], and NO_3^- concentration was derived from Rötliberger et al. [2000].

The NEEM ion concentrations of Na^+ and Ca^{2+} of 50 data from 1282.5 to 1629.65 m, and high resolution data set (dust, Ca^{2+} , Na^+ , NH_4^+ , NO_3^-) of the Holocene and the LGM sections were provided by Fischer et al. [personal communication]. Concentrations of all impurities were measured by continuous flow analysis system at university of Bern. The NEEM SO_4^{2-} concentration of 50 data from 1282.5 to 1629.65 m was provided by Mulvaney et al. [personal communication]. The SO_4^{2-} concentration was measured by ion chromatography at British Antarctic Survey.

Fluxes of ions are derived by multiplying the ion concentration with the reconstructed annual snow accumulation. For the Dome Fuji, the snow accumulation rate is derived from the $\delta^{18}\text{O}$ record [Watanabe et al., 2003a] of the Dome Fuji ice core, following the equation in [Parrenin et al., 2007], and has an uncertainty of 17% for the LGM and 5.3% for the Holocene. The average blank contribution to the SO_4^{2-} concentration equals 1.3% from 25.0 to 16.0 kyr BP and 2.1% from 16.0 to 11.0 kyr BP. For these two periods, the corresponding values for Na^+ are 2.8 and 7.4%, for Ca^{2+} are 5 and 38%, and for Cl^- are 0.5 and 1.8%. For the Dome C, snow accumulation rate is derived from Parrenin et al. [2007]. For the NEEM, snow accumulation rate is derived from Rasmussen et al. [2013]. The uncertainty of snow accumulation rate of NEEM is 10.5% for the Holocene (0.2–11.7 kyr BP) and 29.2% for the last glacial period (11.7–108.1 kyr BP).

2.6 Ion-deduced method

The ice-sublimation method provides only fraction of salts compositions, so the salts concentrations cannot be obtained. To discuss not only fractions of salts compositions but also salts concentrations, the salts concentrations are estimated from the measured ion concentrations. The concentrations of CaSO_4 , Na_2SO_4 , and NaCl salts were calculated from the Ca^{2+} , Na^+ , SO_4^{2-} , Cl^- , and NO_3^- concentrations. I 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 in Chapter 6.

Case I: The Na^+ forms NaCl prior to Na_2SO_4 . This case produces NaCl when the Cl^-/Na^+ ratio is close to the sea-water ratio (1.8 [Whitlow et al., 1992]) as Legrand et al. [1988] and Röthlisberger et al. [2003b] suggested. If $\text{Cl}^-/\text{Na}^+ \geq 1.8$, then

$$[\text{NaCl}] = [\text{Na}^+],$$

$$[\text{Na}_2\text{SO}_4] = 0, \text{ and}$$

$$[\text{CaSO}_4] \text{ equals the smaller of } [\text{Ca}^{2+}] \text{ and } [\text{SO}_4^{2-}].$$

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

$$[\text{NaCl}] = [\text{Cl}^-],$$

$$[\text{Na}_2\text{SO}_4] = 0, \text{ and}$$

$$[\text{CaSO}_4] = [\text{SO}_4^{2-}].$$

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

$$[\text{NaCl}] = [\text{Cl}^-],$$

$$[\text{Na}_2\text{SO}_4] \text{ equals the smaller of } [\text{Na}^+] - [\text{Cl}^-] \text{ and } [\text{SO}_4^{2-}] - [\text{Ca}^{2+}], \text{ and}$$

$$[\text{CaSO}_4] = [\text{Ca}^{2+}].$$

Case II: The Ca^{2+} forms sulfate prior to nitrate, Ca^{2+} forms sulfate prior to Na^+ , and Na^+ forms Na_2SO_4 prior to NaCl . This case is based on ideas from such as Röthlisberger et al. [2003b], Iizuka et al. [2008], and Sakurai et al. [2011]. If $[\text{Ca}^{2+}] > [\text{SO}_4^{2-}]$, I assume

$$[\text{CaSO}_4] = [\text{SO}_4^{2-}],$$

$$[\text{Na}_2\text{SO}_4] = 0, \text{ and}$$

$$[\text{NaCl}] = [\text{Na}^+] + [\text{Ca}^{2+}] - [\text{SO}_4^{2-}] - [\text{NO}_3^-].$$

When this gives $[\text{NaCl}] > [\text{Cl}^-]$, I assume $[\text{NaCl}] = [\text{Cl}^-]$, and

when this gives $[\text{NaCl}] \leq 0$, I assume $[\text{NaCl}] = 0$.

If $[\text{Ca}^{2+}] < [\text{SO}_4^{2-}]$ and $[\text{Ca}^{2+}] + [\text{Na}^+] > [\text{SO}_4^{2-}]$, I assume

$$[\text{CaSO}_4] = [\text{Ca}^{2+}],$$

$$[\text{Na}_2\text{SO}_4] = [\text{SO}_4^{2-}] - [\text{Ca}^{2+}], \text{ and}$$

$$[\text{NaCl}] = [\text{Na}^+] + [\text{Ca}^{2+}] - [\text{SO}_4^{2-}] - [\text{NO}_3^-].$$

Similarly, when this gives $[\text{NaCl}] > [\text{Cl}^-]$, I assume $[\text{NaCl}] = [\text{Cl}^-]$, and

when this gives $[\text{NaCl}] \leq 0$, I assume $[\text{NaCl}] = 0$.

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

$$[\text{CaSO}_4] = [\text{Ca}^{2+}],$$

$$[\text{Na}_2\text{SO}_4] = [\text{Na}^+], \text{ and}$$

$$[\text{NaCl}] = 0.$$

Case III: The Ca^{2+} forms nitrate prior to sulfate. This case is based on an implication of R  thlisberger et al. [2000]. If $[\text{Ca}^{2+}] > [\text{NO}_3^-] + [\text{SO}_4^{2-}]$, I assume

$$[\text{CaSO}_4] = [\text{SO}_4^{2-}],$$

$$[\text{Na}_2\text{SO}_4] = 0, \text{ and}$$

$$[\text{NaCl}] \text{ equals the smaller of } [\text{Na}^+] \text{ and } [\text{Cl}^-].$$

If $[\text{Ca}^{2+}] > [\text{NO}_3^-]$ and $[\text{Ca}^{2+}] + [\text{Na}^+] > [\text{NO}_3^-] + [\text{SO}_4^{2-}]$, I assume

$$[\text{CaSO}_4] = [\text{Ca}^{2+}] - [\text{NO}_3^-],$$

$$[\text{Na}_2\text{SO}_4] = [\text{SO}_4^{2-}] + [\text{NO}_3^-] - [\text{Ca}^{2+}], \text{ and}$$

$$[\text{NaCl}] = [\text{Na}^+] + [\text{Ca}^{2+}] - [\text{SO}_4^{2-}] - [\text{NO}_3^-].$$

When this gives $[\text{NaCl}] > [\text{Cl}^-]$, I assume $[\text{NaCl}] = [\text{Cl}^-]$.

If $[\text{Ca}^{2+}] > [\text{NO}_3^-]$, and $[\text{Ca}^{2+}] + [\text{Na}^+] < [\text{NO}_3^-] + [\text{SO}_4^{2-}]$, I assume

$$[\text{CaSO}_4] = [\text{Ca}^{2+}] - [\text{NO}_3^-],$$

$$[\text{Na}_2\text{SO}_4] = [\text{Na}^+], \text{ and}$$

$$[\text{NaCl}] = 0.$$

If $[\text{Ca}^{2+}] + [\text{Na}^+] < [\text{NO}_3^-]$, I assume that all of the Ca^{2+} and Na^+ are in the form of nitrate:

$$[\text{CaSO}_4] = 0,$$

$$[\text{Na}_2\text{SO}_4] = 0, \text{ and}$$

$$[\text{NaCl}] = 0.$$

If $[\text{Ca}^{2+}] < [\text{NO}_3^-]$ and $[\text{Ca}^{2+}] + [\text{Na}^+] < [\text{NO}_3^-] + [\text{SO}_4^{2-}]$, I assume

$$[\text{CaSO}_4] = 0$$

$$[\text{Na}_2\text{SO}_4] = [\text{Na}^+] + [\text{Ca}^{2+}] - [\text{NO}_3^-], \text{ and}$$

$$[\text{NaCl}] = 0.$$

If $[\text{Ca}^{2+}] + [\text{Na}^+] > [\text{NO}_3^-]$ and $[\text{Ca}^{2+}] + [\text{Na}^+] > [\text{NO}_3^-] + [\text{SO}_4^{2-}]$, I assume

$$[\text{CaSO}_4] = 0$$

$$[\text{Na}_2\text{SO}_4] = [\text{SO}_4^{2-}], \text{ and}$$

$$[\text{NaCl}] = [\text{Na}^+] + [\text{Ca}^{2+}] - [\text{SO}_4^{2-}] - [\text{NO}_3^-].$$

When this gives $[\text{NaCl}] > [\text{Cl}^-]$, I assume $[\text{NaCl}] = [\text{Cl}^-]$.

In a later, I propose a fourth method, Case IV.

2.7 Stable water isotope ratios and time scale

This study uses existing data set of stable water isotope ratios of the Dome Fuji, Dome C and NEEM ice cores. The Dome Fuji $\delta^{18}\text{O}$ records of 212 samples from 329.7 m to 582.7 m were obtained from Watanabe et al. [2003a]. The time scale was determined by the DFO-2006 timescale [Kawamura et al., 2007]. Using $\delta^{18}\text{O}$ placed on the DFGT-2003 [Watanabe et al., 2003a] and DFO-2006 timescale, several fixed points were set and a regression line was set up. The uncertainty is ± 1.3 kyr.

The Dome C $\delta^{18}\text{O}$ records of 672 samples from 201.3 m to 570.4 m were obtained from Stenni et al. [2006]. The time scale was determined by the EDC3 time scale [Parrenin et al., 2007]. The uncertainty is less than ± 1 kyr.

Only the part of the NEEM δD records has been published, I used published NEEM δD records as well as the NGRIP $\delta^{18}\text{O}$ records. The overall features of the NEEM isotope data are very similar to those of NGRIP [Montagnat et al., 2014]. The NEEM records of 410 samples were obtained from Dahl et al. [2013]. The NGRIP $\delta^{18}\text{O}$ records were obtained from Rasmussen et al. [2014] and their references. Both of the NEEM and NGRIP water isotope records are on the GICC chronology.

CHAPTER 3

3 Chemical compositions of non-volatile particles

This chapter examines the major components of chemical compositions of non-volatile particles in the Dome Fuji, Dome C, and NEEM ice cores. In total, 11064 non-volatile particles in the Dome Fuji ice core, 6108 particles in the Dome C ice core, and 35799 particles in the NEEM ice core were analysed. Figure 3.1.1a-d shows examples of typical non-volatile particles of the warm and cold stages of Dome Fuji samples as observed by SEM. Similar shapes of particles were also found from Dome C samples. Figure 3.1.1e-i shows example of typical non-volatile particles of the NEEM observed by SEM. For instance, Particles containing Ca and S are likely to consist mainly of gypsum (Figure 3.1.1e) because these are similar to the SEM image of gypsum [e.g., Badens et al., 1999]. Such needle-like particles are often found in NEEM samples, but rarely seen in Antarctic Dome Fuji samples. However, particles containing Ca and S are not always needle-like shaped. The shapes of the particles shown in Figure 3.1.1e-i are similar but their compositions are different. Therefore, it is difficult to identify the particle compositions based on the shape alone. The samples shown in Figure 1a-i are considered to be NaCl, Na₂SO₄, mixture of silicate mineral and sulfate salt, CaSO₄, silicate mineral, mixture of silicate mineral and sulfate salt, Ca-compound, and NaCl, respectively.

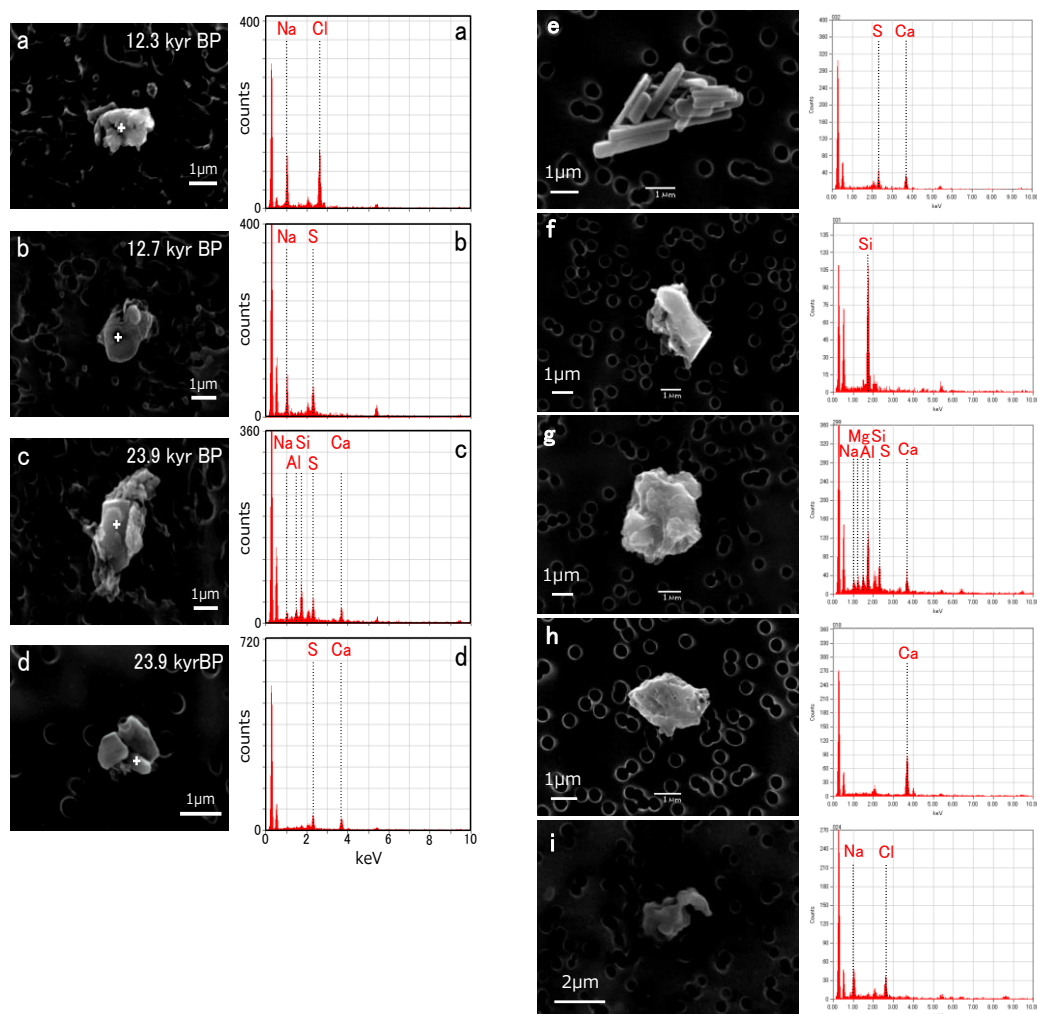


Figure 3.1.1 SEM images and X-ray spectra of particles from warm stages (**a, b**) and cold stages (**c, d**) of the Dome Fuji ice core, and 13.5 kyr BP of the NEEM ice core (**e to i**). (**a**) NaCl from 12.3 kyr BP. (**b**) Na_2SO_4 from 12.7 kyr BP. (**c**) CaSO_4 and silicate mineral from 23.9 kyr BP. (**d**) CaSO_4 from 23.9 kyr BP. (**e**) CaSO_4 particle. (**f**) Silicate particle. (**g**) Mixed particle. (**h**) Ca-particle. (**i**) NaCl particle. The left peak is C (artefact from the filter), the peak second from the left is O, and the peak near 2.0 keV is Pt (artefact from the coating).

3.1 Separating of soluble and insoluble components

To separate the non-volatile particles into soluble and insoluble components, I did a water immersion experiment by following Iizuka et al. [2009]. Since this experiment has already done for the Dome Fuji ice core, and clarified the soluble and insoluble components, this experiment was applied only for the NEEM ice core.

3.1.1 Soluble and insoluble components of Dome Fuji ice core (Antarctica)

This section is review of Iizuka et al. [2009] (Figure 3.1.2). Results from a water immersion experiment of the Holocene and the LGM samples, it was clarified that more than 99% of particles containing S and Cl are water soluble. The Ca containing particles without S and Cl is insoluble. It is considered that particles containing Si are insoluble dust, particles containing S are soluble sulfate salts, and particles containing Cl are soluble chloride salts. The results of the Dome C ice core should be similar to the Dome Fuji results, because behaviours and concentrations of the insoluble dust and ion concentrations are similar to each other on the millennial time scale [e.g., Röthlisberger et al., 2003a; Watanabe et al., 2003b; Fischer et al., 2007; Wolff et al., 2010; Oyabu et al., 2014].

3.1.2 Soluble and insoluble components of NEEM ice core

Figure 3.1.3 shows the number distribution of the elemental compositions in insoluble and non-volatile particles from the Holocene (2.7 kyr BP) and the LGM (19.8 kyr BP) sections. Almost all (> 97%) insoluble particles of both the Holocene and the LGM sections contain Si. Since the major group of insoluble dust in the Greenland ice core are silicates [Maggi, 1997; Svensson et al., 2000], it can be assumed that Si containing particles includes silica minerals. The non-volatile particles of both the Holocene and the LGM sections contain a certain number of S or Cl, whereas the insoluble particles of both sections rarely contain S or Cl. A particle containing S or Cl is considered to be a soluble compound. Since SO_4^{2-} and Cl^- are the major species of soluble ions in the Greenland ice cores [Hansson, 1994; Mayewski et al., 1994; Legrand and Mayewski, 1997], the soluble S or Cl are probably components of sulfate or chloride salts. This scheme of identifying silicate, sulfate and chloride particles is the same as applied by Iizuka et al. [2009] for the Antarctic Dome Fuji ice core (section 3.1.1).

By water immersion, the Na, Mg and K containing non-volatile particle of Holocene section decreased by 5.7, 48.1 and 45.9%, respectively, and by 39.8, 0.0 and 12.3%, respectively, in the LGM sections. The S, Cl and “others” components are mainly dissolved. For Ca containing non-volatile particles show a large depletion after water immersion where Ca containing non-volatile particles in the Holocene and the LGM sections were reduced by 81.0 and 94.5%, respectively. The Ca containing non-volatile particles dissolved not only S, Cl and “others” components but also the Si component suggesting that almost all Ca-particles are water soluble.

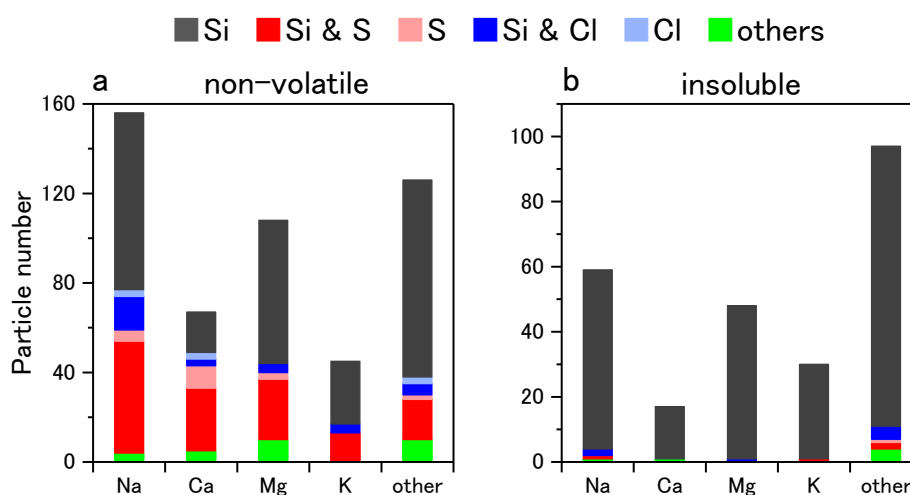


Figure 3.1.2 Number distribution of the elemental compositions of nonvolatile particle and insoluble particle from the LGM section of the Dome Fuji ice core. This figure modified Iizuka et al. [2009]. **(a)** Before water immersing. **(b)** After water immersing. The bars depict Na-, Ca-, Mg- and K- containing particles; “other” particles are particles without Na, Ca, Mg and K. The colors depict combination of Si-, S- and Cl- containing particles. Grey sections indicate particles containing Si but not S or Cl. Blue indicates particles containing Si and Cl but not S. Light blue indicate particles contain Cl but not Si or S. Red indicates particles containing Si and S but not Cl. Light red indicates particles containing S but not Si or Cl. Green indicates particles containing neither Si, Cl nor S.

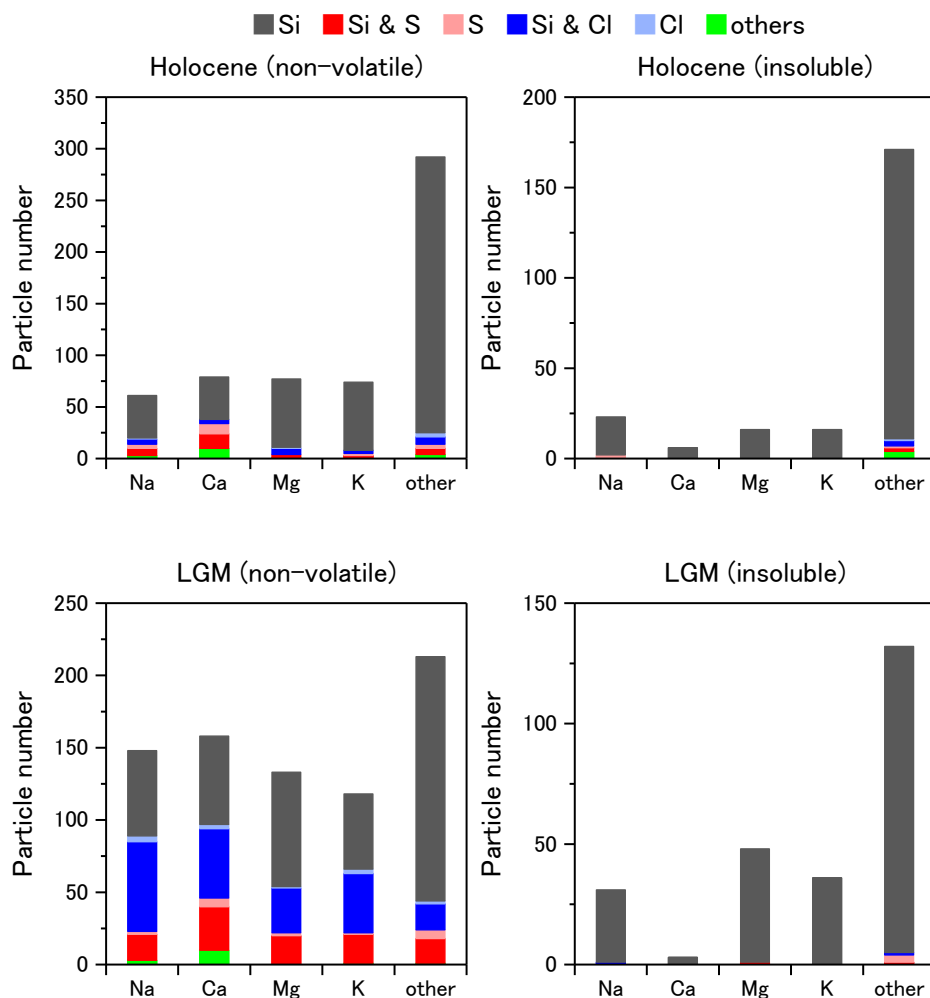


Figure 3.1.3 Number distribution of the elemental compositions of nonvolatile particles and insoluble particles from the Holocene section (2.7 kyr BP) and the LGM section (19.8 kyr BP). The bars depict Na-, Ca-, Mg- and K- containing particles; “other” particles are particles without Na, Ca, Mg and K. The colors depict combination of Si-, S- and Cl- containing particles. Grey sections indicate particles containing Si but not S or Cl. Blue indicates particles containing Si and Cl but not S. Light blue indicate particles contain Cl but not Si or S. Red indicates particles containing Si and S but not Cl. Light red indicates particles containing S but not Si or Cl. Green indicates particles containing neither Si, Cl nor S.

3.2 Elemental combination of non-volatile particles

3.2.1 Number distribution of silicate dust, chloride salts, and sulfate salts

This section examines the combinations of sulfate and chloride particles. The non-volatiles were sorted into 8 categories by focusing on Si (silicate dust), Cl (chloride salts) and S (sulfate salts) (Table 3.1).

3.2.1.1 Dome Fuji ice core

Result of the Dome Fuji ice in 25.0–9.6 kyr BP is shown in Figure 3.2.1a. The Si containing particles account for 80.3% of total particles, and soluble components containing particles account for 53.3 % of total particles. The chloride salts (Cl- and Si-Cl-particles) account for 11.9% of total particles, and 74.8% of them include Si. The sulfate salts (S- and Si-S-particles) account for 30.4% of total particles, and 63.2% of them include Si. The chloride and sulfate salts (Cl-S- and Si-Cl-S-particles) account for 6.9% of total particle, and 79.7% of them include Si. 68.3% of chloride and sulfate salts contain silica minerals.

The Si-Cl-particles are likely mixture of chloride salts and silicate dust. Such mixed particles are formed in the atmosphere when dust particles enter a marine dominated atmosphere [Zhang and Iwasaka, 2001]. The Si-S-particles may be mixture of silicate and sulfate salt, and the Si-Cl-S particle may be mixture of silicate, chloride salt and sulfate salt. Such particles may have experienced contacts or chemical reaction with other during the transportation.

The chloride and sulfate salts account for 92.2% of soluble particles. The number of sulfate salt is twice as large as that of chloride salt, so the sulfate salt is the major soluble salts in the Dome Fuji ice core for 25.0–9.6 kyr BP.

During the last termination (25.0–11.0 kyr BP) at Dome Fuji, the Si containing particle account for 81.2% of total particles, and soluble components containing particles account for 54.8 % of total particles (Figure 3.2.1b). The chloride salts (Cl- and Si-Cl-particles) account for 13.0% of total particles, and 75.9% of them include Si. The sulfate salts (S- and Si-S-particles) account for 30.7% of total particles, and 64.9% of them include Si. The chloride and sulfate salts (Cl-S- and Si-Cl-S-particles) account for 7.7% of total particle, and 80.5% of them include Si. As well as the total particles, the number of chloride and sulfate salts including silica minerals is much larger than that of chloride and sulfate salts without silica minerals. Also, the sulfate salt is the major soluble

salt in the Dome Fuji ice core during the last termination.

3.2.1.2 Dome C ice core

Result of the Dome C ice core for 26.0–6.8 kyr BP is shown in Figure 3.2.1c. The Si containing particle account for 60.1% of total particles, and soluble components containing particles account for 68.9 % of total particles. The chloride salts (Cl- and Si-Cl-particles) account 5.6% of total particle, and 49.6% of them include Si. The sulfate salts (S- and Si-S-particles) account for 46.8% of total particle, and 44.3% of them include Si. The chloride and sulfate salts (Cl-S- and Si-Cl-S-particles) account for 7.6% of total particle, and 71.1% of them include Si. The chloride and sulfate salts account for 87.1% of soluble particles. The number of sulfate salts is more than 4 times larger than that of chloride salts, so the sulfate salt is the major soluble salts in the Dome C ice core for 26.0–6.8 kyr BP.

During the last termination (25.0–10.8 kyr BP) at Dome C, the Si containing particle account for 66.4% of total particles, and soluble components containing particles account for 69.1 % of total particles (Figure 3.2.1d). The chloride salts (Cl- and Si-Cl-particles) account for 5.9% of total particles, and 57.9% of them include Si. The sulfate salts (S- and Si-S-particles) account for 47.7% of total particles, and 53.4% of them include Si. The chloride and sulfate salts (Cl-S- and Si-Cl-S-particles) account for 8.5% of total particles, and 77.4% of them include Si. As well as the total particles, the number of chloride and sulfate salts include silica minerals is much larger than that of chloride and sulfate salts without silica minerals. Also, the sulfate salt is the major soluble salt in the Dome C ice core during the last termination. Compared to the Dome Fuji results, the fraction of sulfate salts is high.

3.2.1.3 NEEM ice core

Result of the NEEM ice in 13X–0.9 kyr BP is shown in Figure 3.2.1e. The Si containing particle account for 84.9% of total particles, and soluble components containing particles account for 49.5 % of total particles. The chloride salts (Cl- and Si-Cl-particles) account for 17.2% of total particles, and 76.4% of them include Si. The sulfate salts (S- and Si-S-particles) account for 19.6% of total particles, and 71.6% of them include Si. The chloride and sulfate salts (Cl-S- and Si-Cl-S-particles) account for 8.5% of total particles, and 85.4% of them include Si. More than 75% of chloride and sulfate salts

contain silica minerals. The chloride and sulfate salts account for 91.5 % of soluble particles. Also the numbers of chloride and sulfate salts are almost same with each other, so the sulfate and chloride salts are the major soluble salts in the NEEM ice core over the last 130 kyr.

During the last termination (25.0–10.8 kyr BP) at NEEM, the Si containing particle account for 86.5% of total particles, and soluble components containing particles account for 49.4 % of total particles (Figure 3.2.1f). The chloride salts (Cl- and Si-Cl-particles) account for 19.1% of total particle, and 76.5% of them include Si. The sulfate salts (S- and Si-S-particles) account for 16.9% of total particle, and 76.5% of them include Si. The chloride and sulfate salts (Cl-S- and Si-Cl-S-particles) account for 9.7% of total particle, and 85.4% of them include Si. As well as total particles, the number of chloride and sulfate salts exists with silica minerals is much larger than that of chloride and sulfate salts without silica minerals. Also the sulfate and chloride salts are the major soluble salts in the NEEM ice core during the last termination.

Table 3.1 Number distribution of the silicate dust, chloride salts, and sulfate salts. Combinations of the sulfate and chloride particles are examined in this section. Non-volatiles were sorted into 8 categories by focusing on Si (silicate dust), Cl (chloride salts) and S (sulfate salts). “T1” in the table indicates a period of the last termination.

			Si	Si∩Cl	Si∩S	Si∩Cl∩S	Cl	S	Cl∩S	other	Total
DF	Total	Number	5163	983	2123	611	331	1236	156	461	11064
		Fraction (%)	46.7	8.9	19.2	5.5	3.0	11.2	1.4	4.2	100
	T1	Number	4188	911	1845	572	290	1000	139	315	9260
		Fraction (%)	45.2	9.8	19.9	6.2	3.1	10.8	1.5	3.4	100
DC	Total	Number	1905	168	1267	329	171	1593	134	541	6108
		Fraction (%)	31.2	2.8	20.7	5.4	2.8	26.1	2.2	8.9	100
	T1	Number	1191	132	984	253	96	858	74	270	3858
		Fraction (%)	30.9	3.4	25.5	6.6	2.5	22.2	1.9	7.0	100
NEEM	Total	Number	18090	4700	5012	2607	1453	1988	445	1504	35799
		Fraction (%)	50.5	13.1	14.0	7.3	4.1	5.6	1.2	4.2	100
	T1	Number	9022	2614	2306	1479	801	708	253	654	17837
		Fraction (%)	50.6	14.7	12.9	8.3	4.5	4.0	1.4	3.7	100

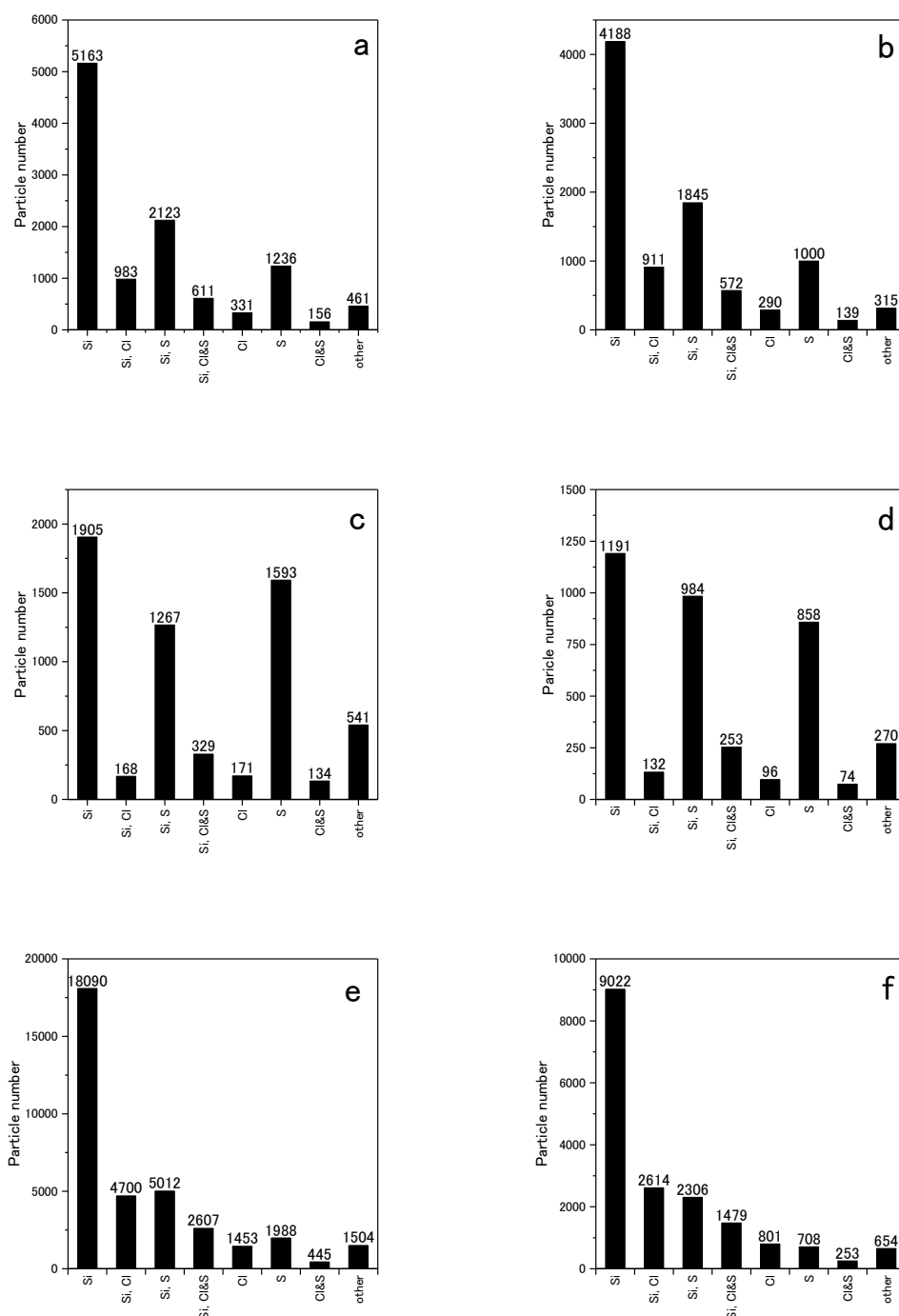


Figure 3.2.1 Number distribution of Si, Cl and S particles from all samples. The Si bar indicates particles containing Si but not S or Cl. The Si-Cl bar indicates particles containing Si and Cl but not S. The Si-S bar indicates particles containing Si and S but not Cl. The Si-Cl-S bar indicates particles containing Si, Cl and S. The Cl bar indicates particles containing Cl but not Si or S. The S bar indicates particles containing S but not Si or Cl. The Cl-S bar indicates particles containing S and Cl but not Si. ‘Other’ bar indicates particles containing neither Si, Cl nor S. (a) 25.0–9.6 kyr BP of DF. (b) 25.0–11.0 kyr BP of DF. (c) 26.0–6.8 kyr BP of DC. (d) 25.0–10.8 kyr BP of DC. (e) Around 130–0.9 kyr BP of NEEM. (f) 25.0–10.8 kyr BP of NEEM.

3.2.2 Chemical compositions of silicate dust, chloride salt and sulfate salt

3.2.2.1 Dome Fuji ice core

Next, the 8 categories were examined based on their content of the 4 elements; Na, Ca, Mg and K. Result of the Dome Fuji ice core for 25.0–9.6 kyr BP is shown in Figure 3.2.2. The most abundant combination of Cl-particle is Na, most likely in the form of sea-salt (NaCl). 60.4% of the Cl-particles is NaCl without any other elements. The most abundant combination of Si-Cl-particle is with Na. 60.5% of Si-Cl-particle contains at least Na. Thus the most dominant chloride salt in the Dome Fuji ice core is NaCl.

The most abundant combination of S-particles is with Na, and the second most abundant combination is with Ca (Figure 3.2.2d, e). This S-Na-particle is probably Na_2SO_4 , and S-Ca-particle is likely to be CaSO_4 . 62.5 and 12.9% of S-particle is Na_2SO_4 and CaSO_4 without any other elements. The most abundant combination of Si-S-particles is with Na, and the second most abundant combination is with Ca. Thus the most dominant sulfate salt is Na_2SO_4 and the second most dominant is CaSO_4 .

The most abundant combination of particles not containing Si, Cl or S (other-particle) is Ca. (Figure 3.2.2h). 80.0% of particles without Si, Cl and S have Ca. There is a possibility that those Ca-particles are CaCO_3 or $\text{Ca}(\text{NO}_3)_2$, but most of the CaCO_3 transported to inland Antarctica is considered to be sulfatized during its transportation [e.g., Kawamura et al., 2003], and the CaCO_3 was found only at the coastal site [Sala et al., 2008]. Thus, particles containing neither Si, Cl nor S with Ca is more likely to be $\text{Ca}(\text{NO}_3)_2$. However, I cannot determine the compositions, because $\text{Ca}(\text{NO}_3)_2$ has not been found yet by micro-Raman measurement. The other-particles containing Ca account for only 3.3% of total particle and not major species, thus I do not treat particles containing neither Si, Cl nor S with Ca as a major soluble salt.

Particles containing Cl and S (Si-Cl-S and Cl-S particle) account for 6.9% of total particles. 79.0% of them include Na, and 43.9% of them include Ca. These Si-Cl-S and Cl-S particles containing Na and/or Ca may be sea-salt particles which are not fully sulfatized, and/or mixture of sea-salt (NaCl) and CaSO_4 .

Particles without Si can be assumed as soluble salt particles by following the water immersion experiment (Figure 3.1.2). Figure 3.2.2i shows number fraction of soluble salt particles for 25.0–9.6 kyr BP. The Na-salt ($\text{NaCl} + \text{Na}_2\text{SO}_4 + \text{other-Na}$) account for 59.5% of total soluble salt particles, thus the Na-salt is the major soluble salts in the Dome Fuji ice core. The major chloride and sulfate salts of

NaCl, Na₂SO₄, and CaSO₄ account for 19.5, 39.0 and 19.1 % of total soluble particles, respectively (Figure 3.2.2i). Thus, the major soluble components of the Dome Fuji ice core for 25.0–9.6 kyr BP are NaCl, Na₂SO₄, and CaSO₄. If I compare the same fraction of the last termination (Figure 3.2.2j) with all measured particles (Figure 3.2.2i), the number fraction of salts is not so different.

3.2.2.2 Dome C ice core

Result of the Dome C ice core for 26.0–6.8 kyr BP is shown in Figure 3.2.3. The most abundant combination of the Cl-particles is with Na, most likely to be NaCl (sea-salt). 59.1% of the Cl-particles is NaCl without any other elements. The most abundant combination of Si-Cl-particles is with Na. 90.0% of the Si-Cl-particles contain at least Na. Thus, the most dominant chloride salt in the Dome C ice core is NaCl as well as the Dome Fuji ice core.

The most abundant combination of the S-particles is with Na, and the second most abundant combination is with Ca. 61.5 and 7.7% of the S-particles is Na₂SO₄ and CaSO₄ without any other elements. The most abundant combination of the Si-S-particles is Na, and the second most dominant is with Ca. Thus, the most dominant sulfate salt in the Dome C ice core is Na₂SO₄ and the second most dominant is CaSO₄, as well as the Dome Fuji ice core.

The abundant combination of particles without Si, Cl and S (other-particle) is Ca (Figure 3.2.3h). 82.2% of particles containing neither Si, Cl nor S have Ca. As well as the Dome Fuji ice, this particle is not major species (7.3% of total particles).

Particles containing Cl and S (Si-Cl-S and Cl-S particle) account for 7.6% of total particles. 94.0% of them include Na, and 54.6% of them include Ca. These Si-Cl-S and Cl-S particles containing Na and/or Ca may be sea-salt particles which is not fully sulfatized and/or mixture of sea-salt (NaCl) and CaSO₄.

Figure 3.2.3i shows number fraction of soluble salt particles for 26.0–6.8 kyr BP. The Na-salt (NaCl + Na₂SO₄ + other-Na) account for 61.0% of the total soluble salt particles, thus the Na-salt is the major soluble salts in the Dome C ice core. The major chloride and sulfate salts of NaCl, Na₂SO₄, and CaSO₄ account for 12.8, 48.2 and 20.1 % of the total soluble particles, respectively (Figure 3.2.3i). Thus, the major soluble components of Dome C ice for 26.0–6.8 kyr BP are NaCl, Na₂SO₄, and CaSO₄. If I compare the same fraction of the last termination (Figure 3.2.3j) with all measured particles (Figure 3.2.3i), number fraction of salts is not so different.

3.2.2.3 NEEM ice core

Result of the NEEM ice core in 13X–0.9 kyr BP is shown in Figure 3.2.4. The most abundant combination of Cl-particles is Na, most likely in the form of NaCl (sea-salt). 56.8% of the Cl-particles is NaCl without any other elements. The most abundant combination of Si-Cl-particle is with Na. 62.5% of Si-Cl-particles contain at least Na. Thus the most dominant chloride salt in NEEM ice is NaCl.

The most abundant combination of S-particles is with Ca, and second most abundant combination is with Na. The S-Ca-particle is probably CaSO_4 , and the S-Na-particle is likely to be Na_2SO_4 . 62.0 and 14.0% of S-particles is CaSO_4 and Na_2SO_4 without any other elements. The most abundant combination of the Si-S-particles is Ca, and the second most dominant is with Na. Thus, the most dominant sulfate salt is CaSO_4 and the second most dominant is Na_2SO_4 .

The most abundant combination of particles not containing Si, Cl or S (other-particle) is Ca. 63.6% of particles without Si, Cl and S have Ca. The Si-particle containing Ca is also considered to be soluble particle (Section 3.1.2). Compounds of this particle cannot be determined from SEM-EDS analysis, but there is a possibility that those Ca-particles are CaCO_3 or $\text{Ca}(\text{NO}_3)_2$ particles of terrestrial origin. This will be discussed in section 3.3.

The composition of Si-Cl-, Si-S, and Si-Cl-S-particles (Figure 3.2.4c, d and g) are more likely to contain multiple elements of Na, Mg, Ca and/or K than particles without Si (Cl-, S- and Cl-S-particle) (Figure 3.2.4b, e, and f).

They are likely mixture of chloride/sulfate salts and silicate dust. The proportion of Si-Cl-particles having not only Na but also Mg, Ca and/or K is higher than that of Cl-particles, and that of Si-S-particle having not only Ca but also Na, Mg, and/or K is also higher than for S-particles. The Si-Cl-particles having multiple elements of Na, Mg, Ca and/or K accounts for 51.6% of the total Si-Cl-particles, whereas the corresponding number is 40.6% for Si-S-particles. The proportion of Si-Cl-S-particle having multiple elements is higher than for Si-Cl- and Si-S-particles (Figure 3.2.4g). The percentage of Si-Cl-S-particles containing multiple elements of Na, Mg, Ca and/or K is 75.5%. Such multiple compositions indicate that the particles have experienced several contacts or chemical reaction with other particles such as silicate, H_2SO_4 [e.g., Legrand and Delmas, 1988], NaCl [e.g., Legrand and Delmas, 1988], KCl, [e.g., Popovicheva et al., 2014], CaSO_4 and/or CaCO_3 [e.g., Legrand and Mayewski, 1997] during the transportation.

Particles without Si, and particles containing Ca can be considered as soluble salt particles

according to the water immersion experiment (Figure 3.1.3). Figure 3.2.4i shows number fraction of soluble salt particles over the last 130 kyr. The Ca-salt (other-Ca + CaSO_4 + Ca-Cl particle) and Na-salt (NaCl + Na_2SO_4 + other-Na) account for 89.0% of the total soluble salt particles, thus the Ca-salt and Na-salt are the major soluble salts in the NEEM ice core. The NaCl , Na_2SO_4 , CaSO_4 , and Ca-particles without S and Cl (other-Ca) account for 23.5, 16.0, 25.1, and 16.2 % of the total soluble particles, respectively (Figure 3.2.4i). Thus the major soluble components of the NEEM ice core for the last 130 kyr are NaCl , Na_2SO_4 and CaSO_4 , and other-Ca. If I compare the same fraction of the last termination (Figure 3.2.4j) with all measured particles (Figure 3.2.4i), number fraction of salts is not so different.

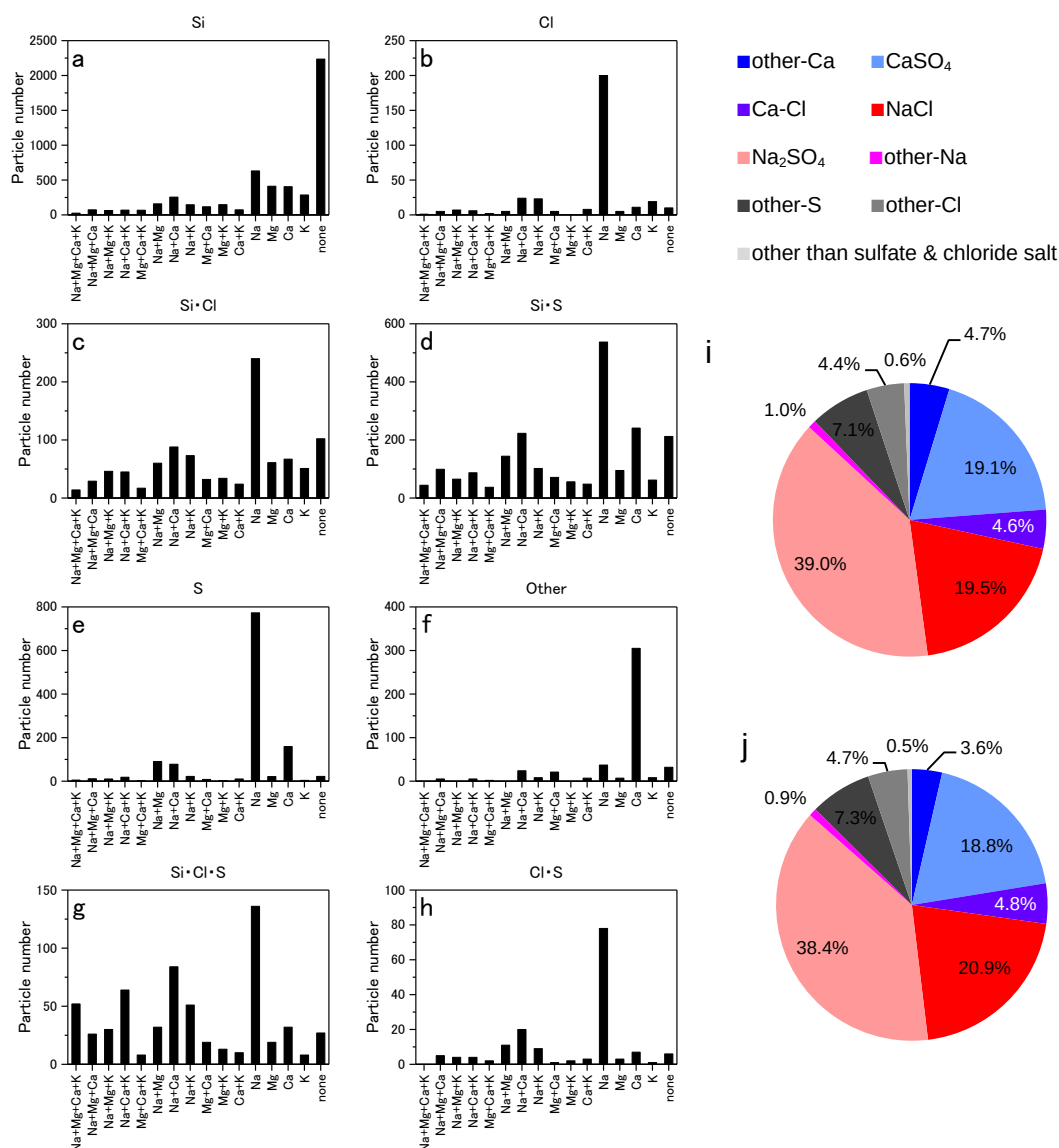


Figure 3.2.2 Dome Fuji. Number distribution of Si, Cl and S particles focusing on Na, Mg, Ca and K. **(a)** Particle containing Si but not Cl or S. **(b)** Particle containing Cl but not Si or S. **(c)** Particle containing Si and Cl but not S. **(d)** particle containing Si and S but not Cl. **(e)** Particle containing S but not Si or Cl. **(f)** Particle containing neither Si, Cl nor S. **(g)** Particles containing Si, Cl and S. **(h)** Particles containing Cl and S but not Si. **(i)** Number fraction of soluble components of the particles from all period (25.0–9.6 kyr BP). **(j)** The same as **i** except that is shown the last termination (25.0–11.0 kyr BP).

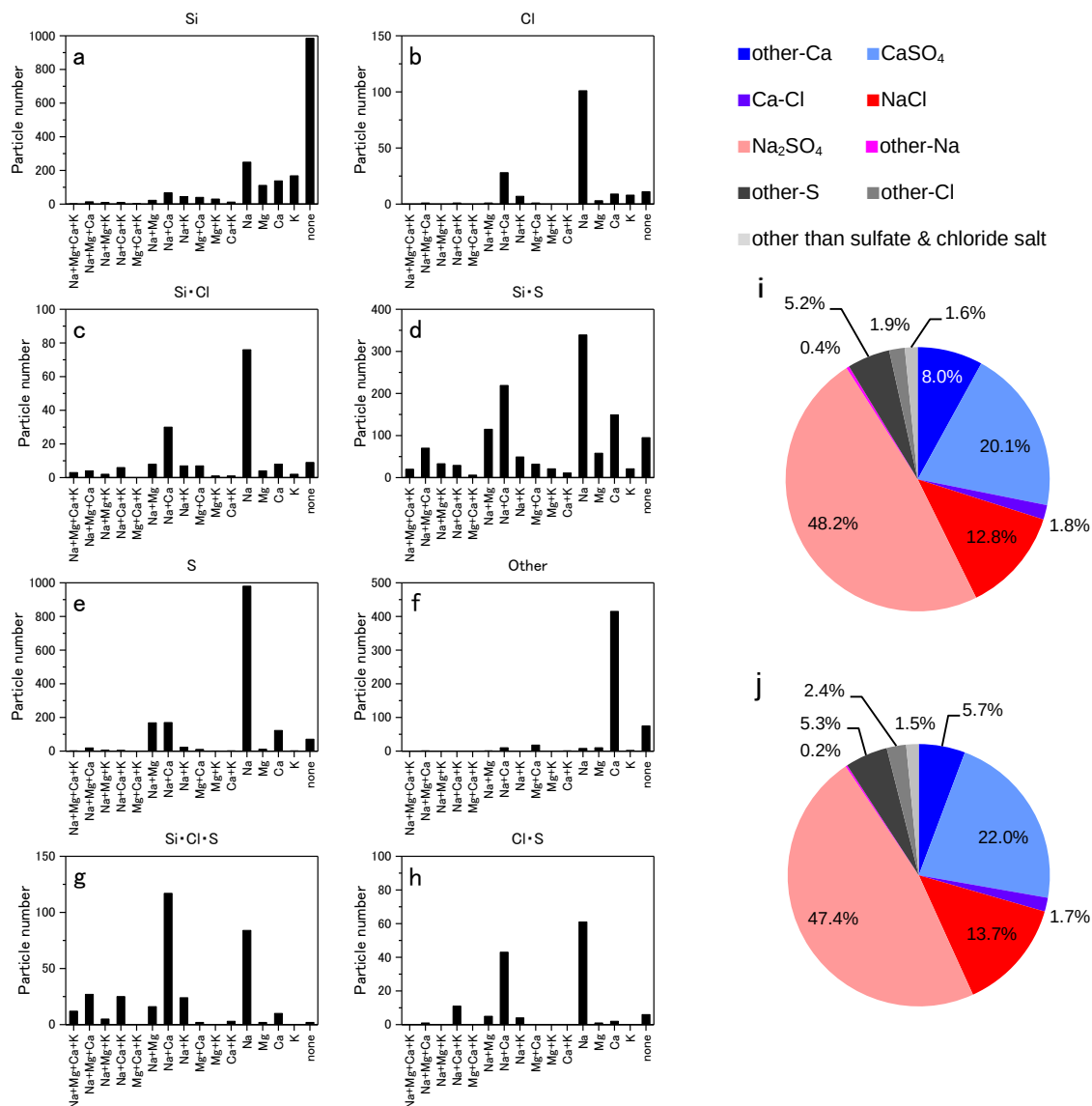


Figure 3.2.3 Dome C. Number distribution of Si, Cl and S particles focusing on Na, Mg, Ca and K. (a) Particle containing Si but not Cl or S. (b) Particle containing Cl but not Si or S. (c) Particle containing Si and Cl but not S. (d) particle containing Si and S but not Cl. (e) Particle containing S but not Si or Cl. (f) Particle containing neither Si, Cl nor S. (g) Particles containing Si, Cl and S. (h) Particles containing Cl and S but not Si. (i) Number fraction of soluble components of the particles from all period (26.0–6.8 kyr BP). (j) Same as i except that is shown the last termination (26.0–11.0 kyr BP).

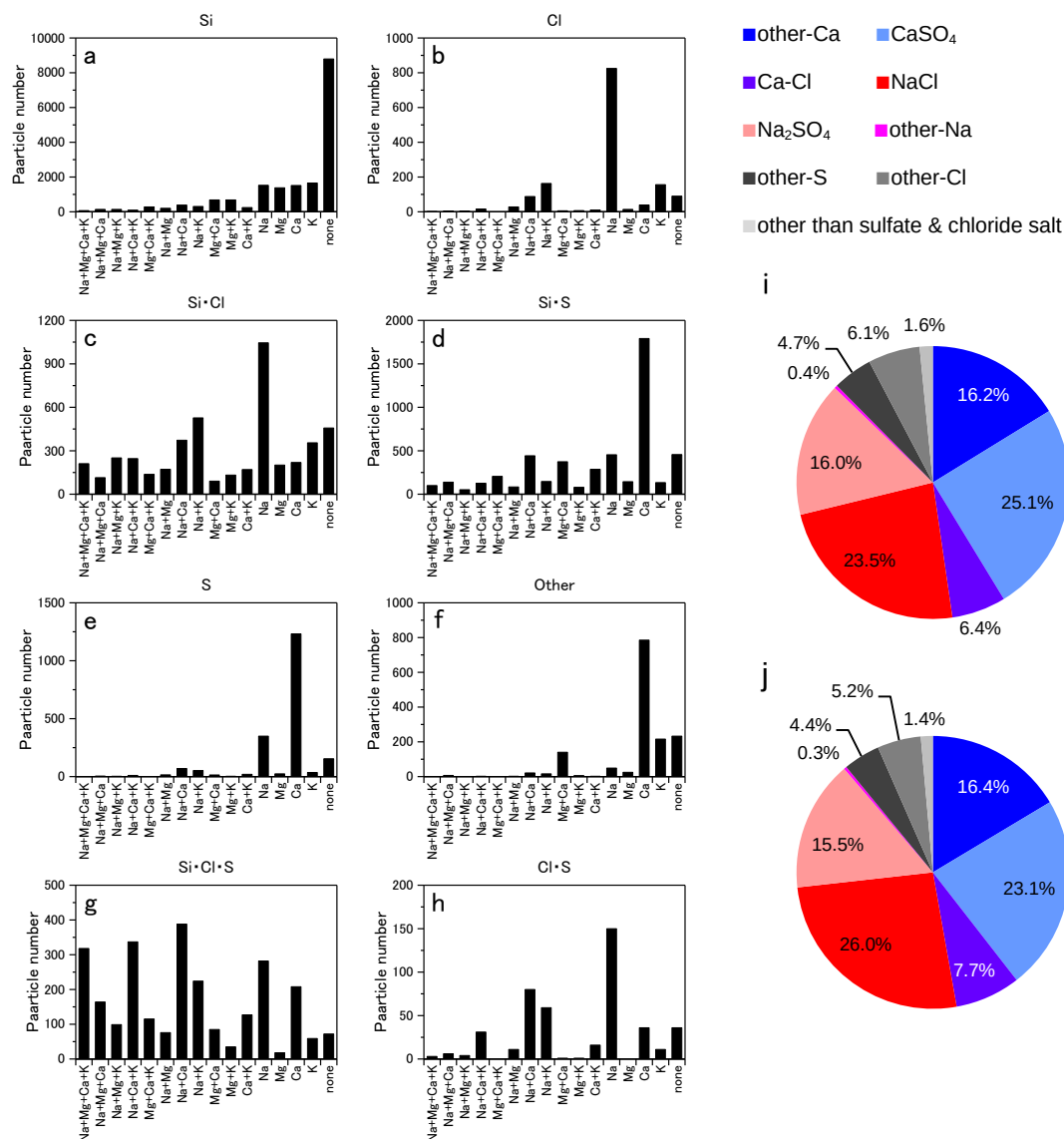


Figure 3.2.4 NEEM. Number distribution of Si, Cl and S particles focusing on Na, Mg, Ca and K. (a) Particle containing Si but not Cl or S. (b) Particle containing Cl but not Si or S. (c) Particle containing Si and Cl but not S. (d) particle containing Si and S but not Cl. (e) Particle containing S but not Si or Cl. (f) Particle containing neither Si, Cl nor S. (g) Particles containing Si, Cl and S. (h) Particles containing Cl and S but not Si. (i) Number fraction of soluble components of the particles from all period (before Eemian-0.9 kyr BP). (j) Same as i except that is shown the last termination (26.0–8.9 kyr BP).

3.2.3 Short summary and bipolar comparison

The dominant soluble salts in the Dome Fuji, Dome C and NEEM ice cores are sulfate salts and chloride salts. The number of sulfate salts is larger than that of chloride salt in the Dome Fuji and Dome C ice cores. In contrast, the number of chloride salts is almost the same with that of sulfate salts in the NEEM ice core. The major soluble salt particles are NaCl, Na₂SO₄, and CaSO₄ in the Dome Fuji and Dome C ice cores, and NaCl, Na₂SO₄, CaSO₄ and other-Ca in the NEEM ice core. The dominant sulfate salt in inland Antarctica is Na₂SO₄ and second most dominant is CaSO₄, whereas the dominant sulfate salt of the NEEM ice core is CaSO₄ and second most dominant is Na₂SO₄. The Na₂SO₄ originates from primary NaCl (sea-salt) that is neutralized in the atmosphere [Legrand and Delmas, 1988], whereas the CaSO₄ originates from primary CaCO₃ that is neutralized in the atmosphere and from direct dust emission in the form of gypsum [Legrand et al., 1997]. . Namely, the contribution of the sea-salt is higher in Antarctica than in Greenland. The higher contribution of the sulfate salt and sea-salt in the Antarctic ice cores may be because inland Antarctic ice sheet has highly contribution of sea-salt and SO₄²⁻ from the southern ocean, and sulfatization was enhanced. The higher contribution of the terrestrial salt in the NEEM ice core may be because the Greenland ice sheet has highly contribution of terrestrial material. Also, the higher contribution of the chloride salt in NEEM ice core indicates that larger proportion of sea-salt came to central Greenland without being oxidized by H₂SO₄ or HNO₃. More detailed discussion will be described in Chapter 5.

3.3 Identifying the calcium compounds by Raman-EDS analysis

The carbonates, such as CaCO_3 , are one of the major components of mineral dust and are known to be reactive with H_2SO_4 and HNO_3 [Liu et al., 2008]. It has been suggested that the CaCO_3 and $\text{Ca}(\text{NO}_3)_2$ are deposited on the Greenland ice sheet [e.g., Mayewski et al., 1994; De Angelis et al., 1997; Röthlisberger et al., 2002], and Sakurai et al. [2009] identified CaCO_3 in the GRIP ice core. As described in sections 3.1 and 3.2, a high amount of soluble Ca particles other than CaSO_4 (Ca-particle without S and Cl) was found. To determine the chemical compounds of “Ca-particle without S and Cl”, the results of a micro-Raman measurement were compared to that of the SEM-EDS measurement.

Several sharp Raman spectra were observed from non-volatile particles (Figure 3.3.1). To identify the species, I compared these results with reference spectra of the specimens. The specimens of CaCO_3 showed a major peak at 1086 cm^{-1} (from the C-O symmetric stretching mode) and a secondary peak at 712 cm^{-1} from other modes. The $\text{CaMg}(\text{CO}_3)_2$ (dolomite) showed a major peak at 1095 cm^{-1} (from the C-O symmetric stretching mode) and a secondary peak at 723 cm^{-1} . The $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ showed at 1051 cm^{-1} (from the N-O symmetric stretching mode) and the weak peaks at 743 and 1353 cm^{-1} . The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ showed major peak at 1008 cm^{-1} (from the S-O symmetric stretching mode) and the secondary peaks at 415 , 493 , 620 , and 670 cm^{-1} . Silica minerals shows the bands between 100 and 600 cm^{-1} , predominant are the vibrations of Si-O-Si, being followed by bending of Si-O-Si or O-Si-O angles [Kihara et al., 2005].

As shown in Figure 3.3.1a–d, the observed spectra appeared at similar positions of references of CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, so those minerals are present in the glacial sections of the NEEM ice core. In particular, $\text{CaMg}(\text{CO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ are found in the Greenland ice cores for the first time. I also found many particles showing the strong bands between 100 and 600 cm^{-1} , which are probably silica minerals (e.g., Figure 3.3.1e). Among 423 particles, 39 of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 21 of CaCO_3 , 5 of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 2 of $\text{CaMg}(\text{CO}_3)_2$, and 147 of silica minerals were detected (Figure 3.3.2a). The number ratio of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to the sum of CaCO_3 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{CaMg}(\text{CO}_3)_2$ is 1.39 ± 0.35 . The CaSO_4 exist about 1.4 more often as the sum of CaCO_3 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{CaMg}(\text{CO}_3)_2$.

Those samples were also observed by SEM-EDS. I made a classification based on the elemental compositions of non-volatile particles as follows; if a particle contain Ca and S, it is classified as CaSO_4 ; if a particle contains Ca, no S and no Cl, it is classified as $\text{CaCO}_3 + \text{Ca}(\text{NO}_3)_2$; if a particle contains Ca, Mg, no S and no Cl, it is classified as $\text{CaMg}(\text{CO}_3)_2$; if a particle contains Na and Cl, it is

classified as NaCl; if a particle contains Na and S, it is classified as Na₂SO₄; if a particle contains S, no Ca and no Na, it is classified as other-S; if a particle contains Cl and no Na, it is classified as other-Cl, and if a particle does not contain any Si, S, Cl or Ca, it is classified as ‘other’. The Si containing particles are classified as silicate minerals. In total, 414 particles were measured: 45 of CaSO₄, 32 of CaCO₃ + Ca(NO₃)₂, 19 of CaMg(CO₃)₂, 62 of NaCl, 18 of Na₂SO₄, 1 of other-S, 13 of other-Cl, 11 of ‘other’, and 382 silica minerals were detected (Figure 3.3.2b). The number ratio of CaSO₄ to sum of CaCO₃, Ca(NO₃)₂ and CaMg(CO₃)₂ is 0.88 ± 0.33 . This ratio agrees with that of the micro-Raman measurement within error estimates. The sum of CaCO₃, Ca(NO₃)₂ and CaMg(CO₃)₂ particles corresponds to “Ca-particle without S and Cl (other-Ca)” classified in section 3.2. Thus, “Ca-particle without S and Cl” can be considered as CaCO₃, Ca(NO₃)₂ and/or CaMg(CO₃)₂. As Figure 3.3.2b shows, CaCO₃ accounts for 75.0% of the sum of CaCO₃, Ca(NO₃)₂•4H₂O and CaMg(CO₃)₂, and CaCO₃ is the dominant component in these three salts. Therefore, “Ca-particle containing neither S nor Cl” can be regarded as CaCO₃.

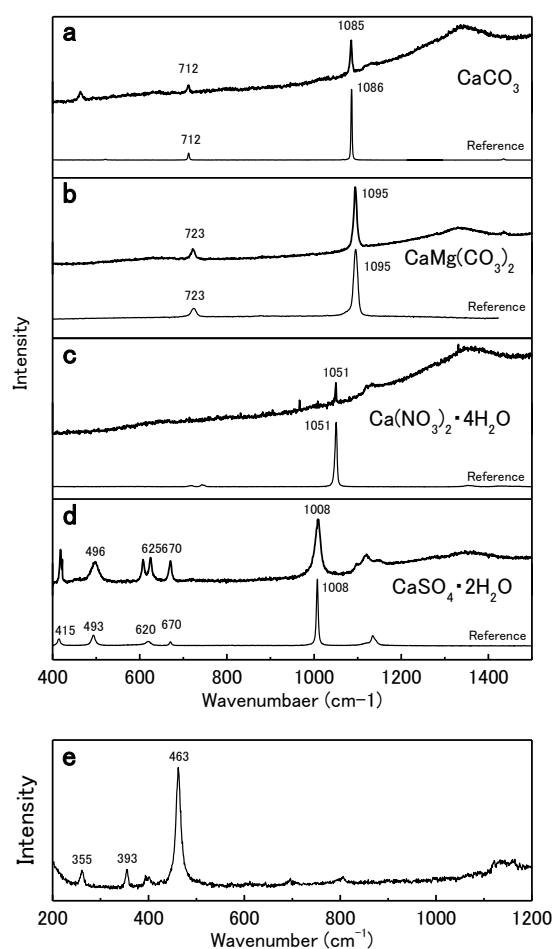


Figure 3.3.1 Raman spectra from 400-1500 cm⁻¹ (a-d) and from 200-1200cm⁻¹ (e). Each panel shows observed spectra of non-volatile particles of the LGM sections (upper) and reference data (bottom). (a) CaCO_3 . (b) $\text{CaMg}(\text{CO}_3)_2$ (dolomite). $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. (d) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. (e) Example of silicate mineral.

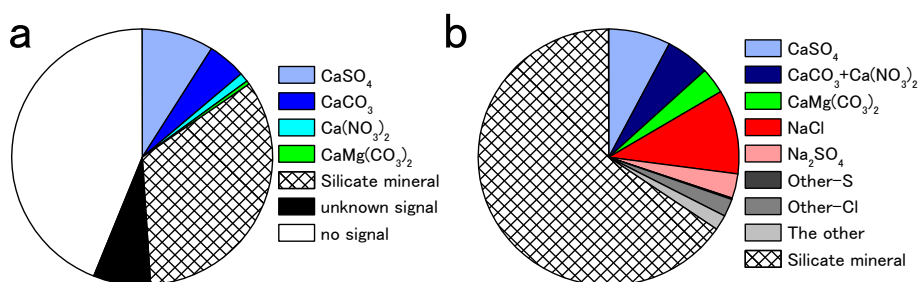


Figure 3.3.2 Number fraction of particles of glacial sections measured by the micro-Raman spectroscopy spectrometer and the SEM-EDS. (a) Number fraction of particles analyzed by the micro-Raman spectrometer. The particles showing bands between 100–600 cm⁻¹ are classified as ‘silicate minerals’. Particles showing spectra that could not be identified are indicated as ‘unknown signal’. Particle showing no spectral features are classified as ‘no Raman signal’. (b) Number fraction of particles analyzed by SEM-EDS. Classification of particles is written in body text.

3.4 Time series variations of major sulfate and chloride salts in inland Antarctica

Results in the section 3.2 showed that the major soluble components of the Dome Fuji and Dome C ice cores are CaSO_4 , Na_2SO_4 , and NaCl . In this section, time series variations of those major soluble components in inland Antarctica are examined.

3.4.1 Comparison of sulfate salts compositions in the Dome Fuji ice core using the sublimation-EDS and micro-Raman methods

To evaluate the abundance of sulfate salts obtained from the sublimation-EDS method, I compare the number ratio of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ of Dome Fuji obtained from the sublimation-EDS method with that from 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 the datapoint at 24.7 kyr BP, the number ratio of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ from the sublimation-EDS method agrees with that of the micro-Raman method (Figure 3.4.1). The sublimation-EDS method gives 0.92 ± 0.40 from 25.0 to 17.3 kyr BP, whereas the micro-Raman method gives 0.04 at 24.7 kyr BP and 0.79 at 19.3 kyr BP. The average ratio from the sublimation-EDS method after 16.8 kyr BP is 3.27 ± 1.76 . For the micro-Raman method, the ratios at 16.8, 14.3, 12.9 and 11.2 kyr BP are 1.53, 3.91, 4.09 and 5.40, respectively. Thus, the sublimation-EDS method reconstructs 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 the sublimation conditions (-50°C , 0.55 MPa), H_2SO_4 remains liquid, HNO_3 remains solid, whereas HCl becomes a volatile gas [Ohe, 1976; Kulmala and Laaksonen, 1990; Luo et al., 1995; Marion, 2002]; however, reaction between HCl gas and the particle is unlikely under the method's non-equilibrium conditions. The H_2SO_4 also should not affect the particles during sublimation because the H_2SO_4 is likely still on the ice-crystal surfaces, away from the particles in the interior. In fact, in the ice core, the H_2SO_4 collects at grain boundaries [e.g., Fukazawa et al., 1998], whereas the solid particles are within grains [Ohno et al., 2005]. The sublimation process is about 100 hours, during which the H_2SO_4 has plenty of time to flow through the filter. I 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 .

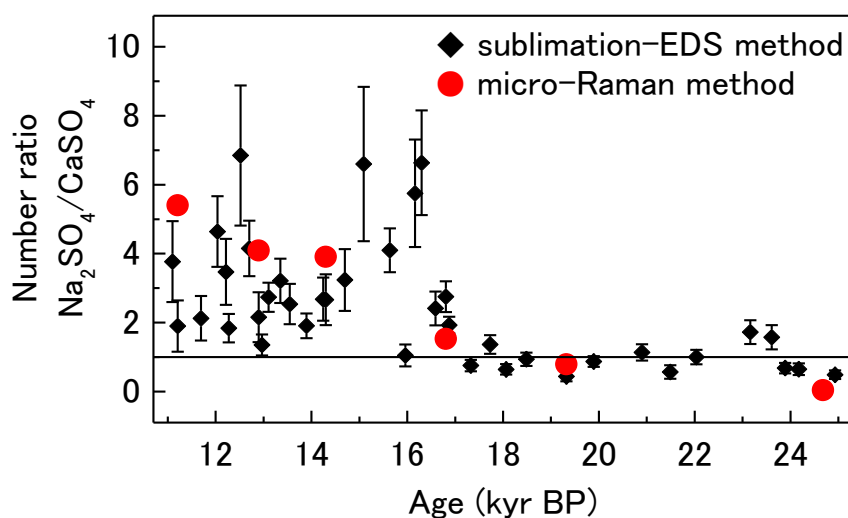


Figure 3.4.1 Number ratio of Na_2SO_4 to CaSO_4 of Dome Fuji. Black dots indicate the ratio from the sublimation-EDS method and red dots indicate that from the micro-Raman method [Sakurai et al., 2011]. The horizontal line indicates 1.

3.4.2 Time series changes of the insoluble and major soluble components in the Dome Fuji ice core

Figure 3.4.2a shows the time series ratio of the Si containing particle (insoluble particle) to the total particles. During 25.0–16.6 kyr BP, $94.1 \pm 3.1\%$ of particles contain Si. The ratio for 16.6–12.0 kyr BP shows large variability (29–96%) with an average ratio of $72.1 \pm 17.0\%$. After 12.0 kyr BP, the ratio slightly increased ($76.3 \pm 8.9\%$). The significant decreasing of dust concentration from the LGM increased the ratio of non-volatile particle without Si (mainly soluble particle).

Figure 3.4.2b shows the time series of the soluble particles fraction. Focusing on the major soluble particle of Na_2SO_4 , CaSO_4 and NaCl , the fractions between 25.0 and 16.6 kyr BP are similar to each other (CaSO_4 is 25.8 ± 7.8 , Na_2SO_4 is 28.0 ± 8.2 and NaCl is 22.5 ± 8.0 %). For 16.3–11.0 kyr BP, the fractions of CaSO_4 and NaCl decreased (10.6 ± 3.9 and 16.0 ± 9.8 %), and Na_2SO_4 fraction increased (43.5 ± 15.5 %). In the Holocene period (11.0–9.6 kyr BP), the fraction of CaSO_4 increased (the fraction of CaSO_4 , Na_2SO_4 and NaCl is 17.1 ± 9.2 , 37.7 ± 22.2 , and 9.2 ± 8.5 %, respectively).

3.4.3 Time series changes of the insoluble and major soluble components in the Dome C ice core

Figure 3.4.3a shows the time series ratio of the Si containing particle (insoluble particle) to the total particles. In 25.0–18.2 kyr BP, $86.4 \pm 4.9\%$ of particles contain Si. The ratio starts to decrease after 18.2 kyr BP, and reaches low Holocene level at 14.5 kyr BP. After 12.0 kyr BP, the ratio slightly increased as well as the Dome Fuji ice core. The ratio for 14.5–6.8 kyr BP shows $48.1 \pm 10.5\%$. Timing when the ratio started to decrease is almost the same as the Dome Fuji ice core. The dust concentration started to decrease from the LGM level at around 17.3 kyr BP [Röthlisberger et al., 2003a]. The ratio of the Dome C ice core after 18.2 kyr BP is lower than that of the Dome Fuji ice core, but the changing way is similar to each other. The ratio around 12.0 kyr BP shows a minimum value both in the Dome Fuji and Dome C ice cores, then the ratio slightly increased after that. These timing of the changes in the Dome C ice core correspond to those in the Dome Fuji ice core within the margin of dating error.

Figure 3.4.3b shows the time series of the soluble particles fraction. Focusing on the major soluble particle of Na_2SO_4 , CaSO_4 and NaCl , the fractions between 25.0 and 18.2 kyr BP have 27.1 ± 3.8 for CaSO_4 , 38.2 ± 9.8 for Na_2SO_4 , and $20.6 \pm 9.5\%$ for NaCl . During 16.9–11.3 kyr BP, the fractions of CaSO_4 and NaCl decreased (15.8 ± 5.6 and $9.5 \pm 4.7\%$), and Na_2SO_4 fraction increased ($55.2 \pm 9.5\%$). In the Holocene period (10.8–6.8 kyr BP), the fraction of CaSO_4 and NaCl slightly increased (the fraction of CaSO_4 , Na_2SO_4 and NaCl is 16.9 ± 5.6 , 49.9 ± 7.6 , and $10.2 \pm 7.5\%$, respectively). This trend is similar to that of the Dome Fuji ice core, but the fraction of Na_2SO_4 in the Dome C ice core is higher than that of the Dome Fuji ice core through the whole period of the last termination (25.0–11.0 kyr BP).

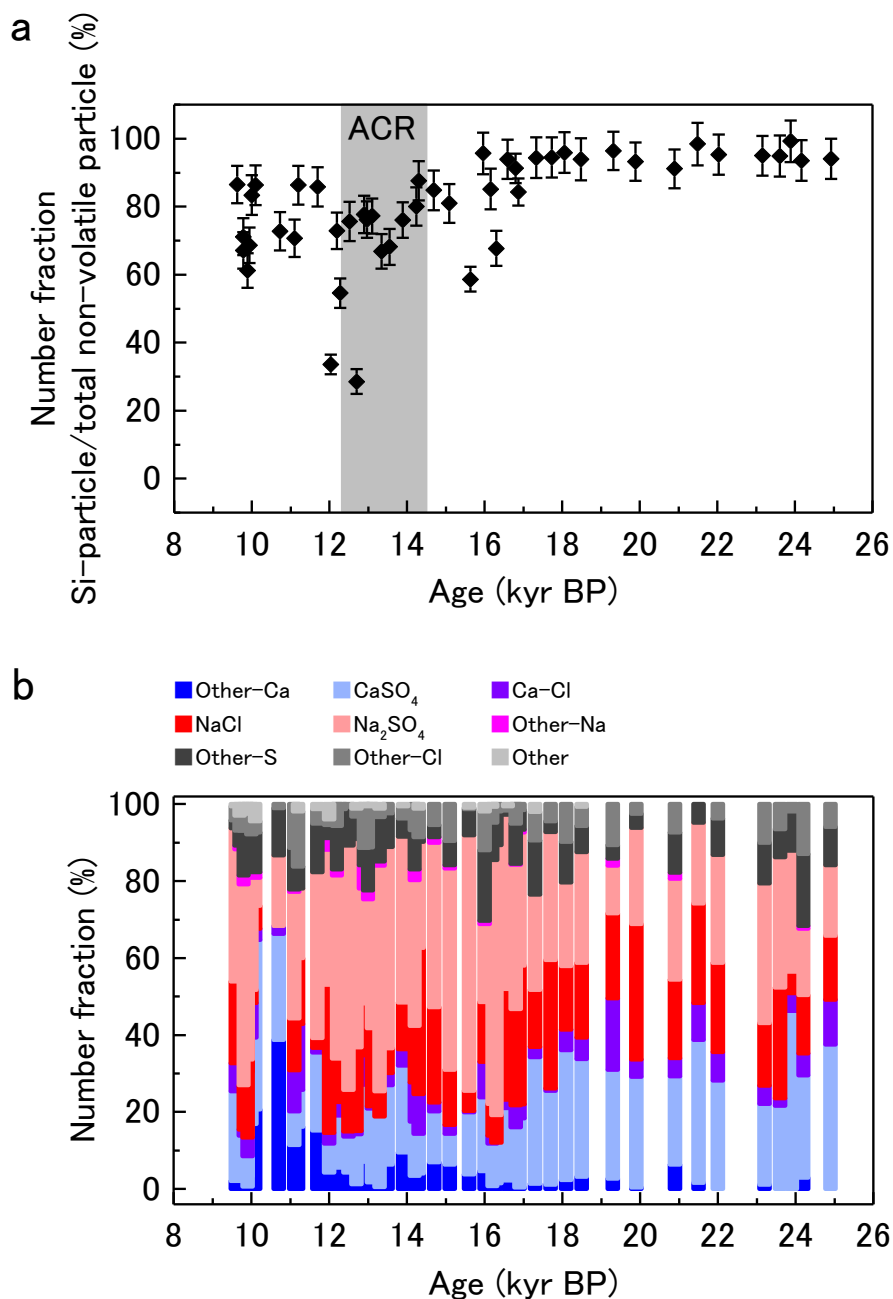


Figure 3.4.2 (a) Number ratio of Si-containing particles to total non-volatile particles in the Dome Fuji ice core. (b) Time-series number fraction of soluble components of the Dome Fuji ice core. Other-Ca indicates particles containing Ca but not Si, S nor Cl. Ca-Cl indicates particles containing Ca and Cl. Other-Na indicates particles containing Na but not Si, S or Cl. Other-S indicates sulfate salts other than Na₂SO₄ and CaSO₄. Other-Cl indicates chloride salts other than NaCl and Ca-Cl particles. 'Other' indicates soluble salts other than sulfate and chloride salts. Gray shades indicates Younger Dryas, LGM, and glacial stadials.

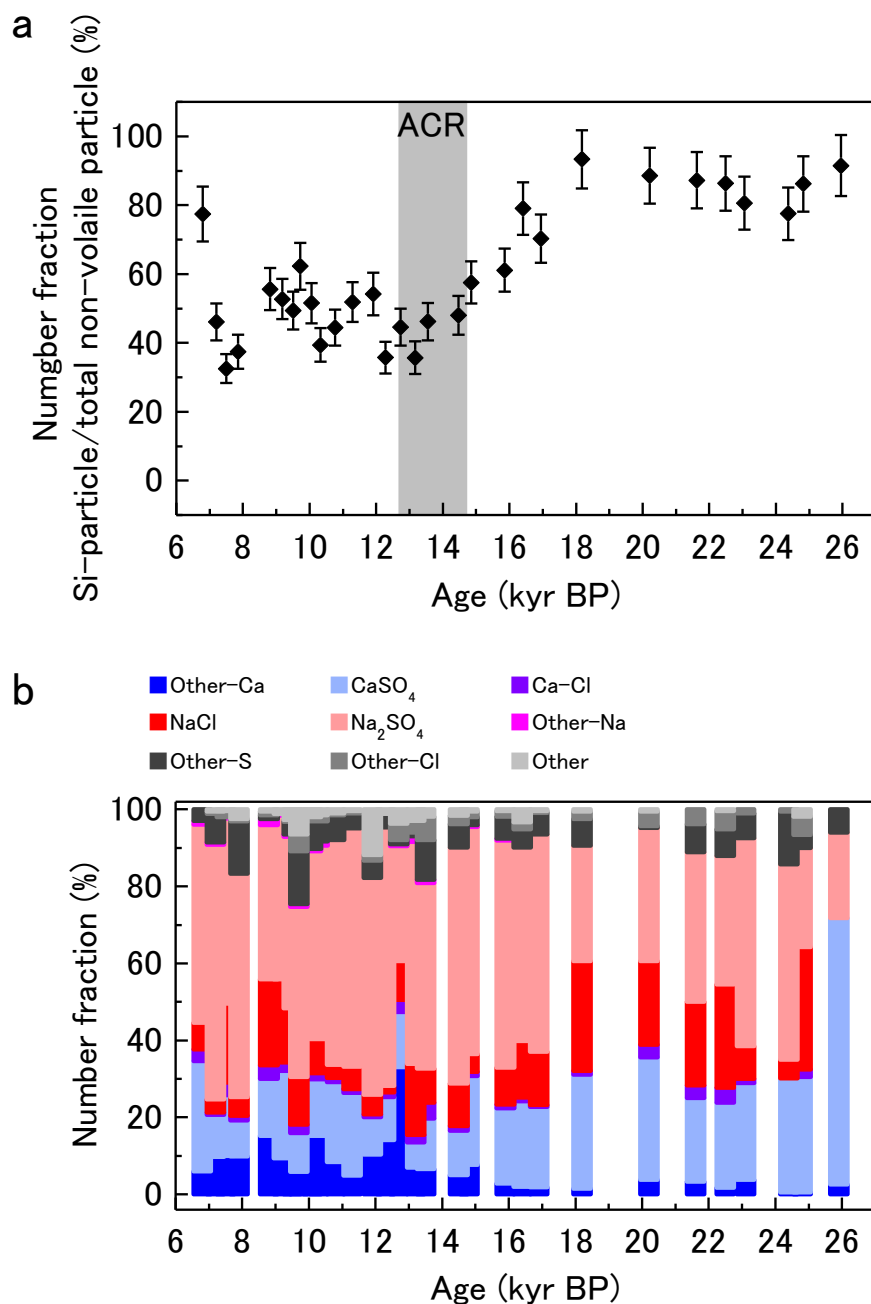


Figure 3.4.3 (a) Number ratio of Si-containing particles to total non-volatile particles in the Dome C ice core. (b) Time-series number fraction of soluble components of the Dome C ice core. Other-Ca indicates particles containing Ca but not Si, S nor Cl. Ca-Cl indicates particles containing Ca and Cl. Other-Na indicates particles containing Na but not Si, S or Cl. Other-S indicates sulfate salts other than Na₂SO₄ and CaSO₄. Other-Cl indicates chloride salts other than NaCl and Ca-Cl particles. ‘Other’ indicates soluble salts other than sulfate and chloride salts. Gray shades indicates Younger Dryas, LGM, and glacial stadials.

3.5 The major sulfate and chloride salts in Greenland

Results in the section 3.2 showed that the major soluble components of the NEEM ice core are NaCl, Na₂SO₄, CaSO₄, and other-Ca (CaCO₃ in glacial period). This section examines the time series variations of those major soluble components in Greenland.

3.5.1 Time series changes of the insoluble and major soluble components in the NEEM ice core

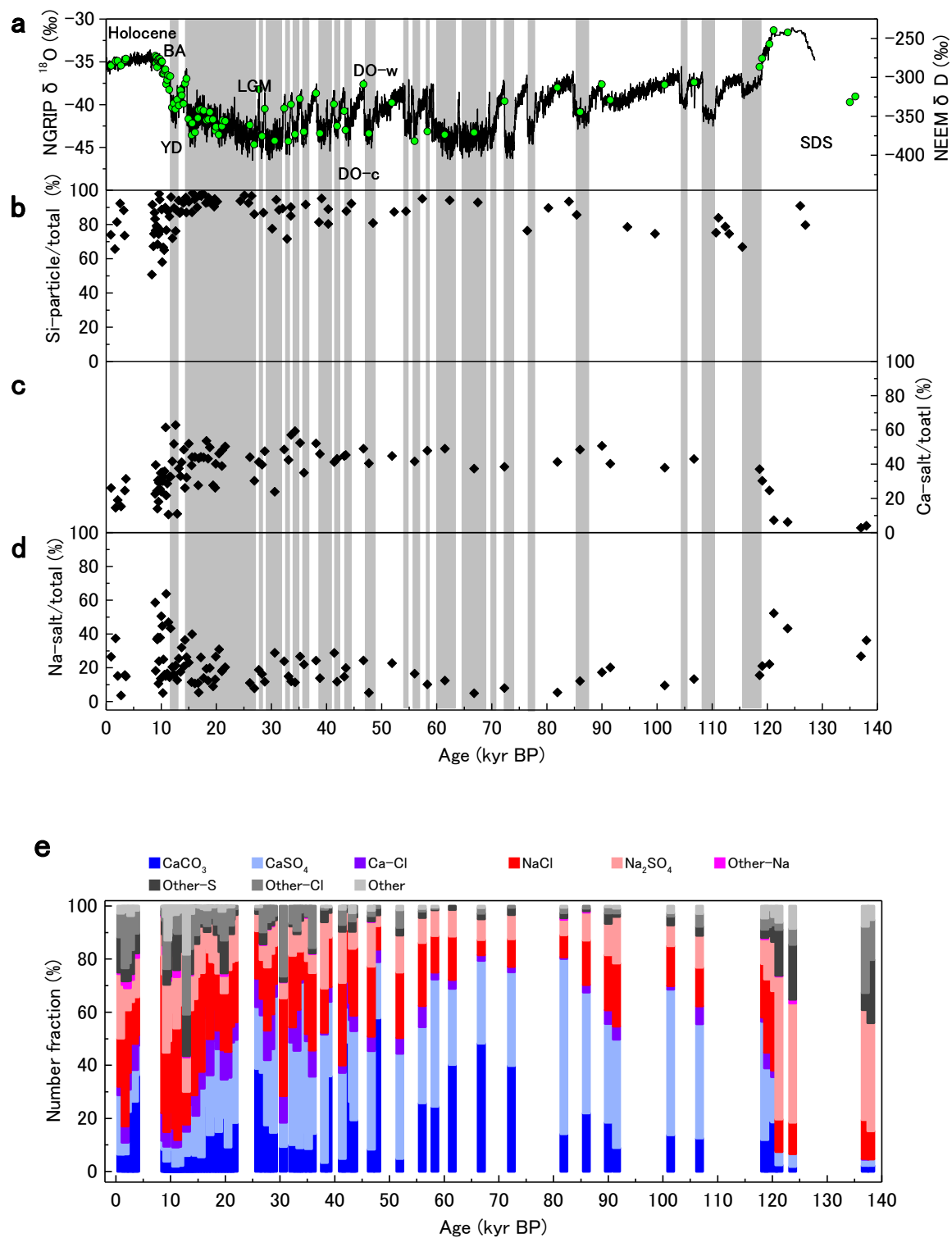
Climatic stages are divided into 7 categories; the Holocene, the Younger Dryas (YD), the Bølling-Allerød (BA), the Last Glacial Maximum (LGM), warm periods of Dansgaard-Oeschger events (DO-w), cold periods of Dansgaard-Oeschger events (DO-c), and the Stratigraphic Disruptions Section (SDS).

Figure 3.5.1b–d shows the time series ratio of Si containing particles (insoluble dust) to total particles, Ca-salts to total non-volatile particles and Na-salts to total non-volatile particles. The average number ratio of Si-particle to total non-volatile particles is 77.7, 89.5, 84.9, 93.7, 83.6, 91.7, and 78.6% for Holocene, YD, BA, LGM, DO-w, DO-c, and SDS, respectively. The ratio of Si-particle/total is higher in glacial period than in the Holocene and the SDS. In glacial period, the ratio is higher in the colder stages of the LGM and the DO-c than that in milder stages of the YD and the DO-w. This indicates that the contribution of terrestrial dust particles to total non-volatile aerosols is higher in colder climate stages.

The average number ratio of Ca-salt to total non-volatile particle is 24.8, 44.4, 28.8, 36.7, 40.8, 38.0, and 16.0% in the Holocene, YD, BA, LGM, DO-w, DO-c, and SDS, respectively. The ratio of Ca-salt/total is higher in the colder stages of the YD, LGM, DO-w, and DO-c than in the warmer stages of the Holocene, BA and SDS. Looking into the last glacial period, Ca-particle/total in milder stages of the YD and the DO-w are higher than in the colder stages of the LGM and the DO-c, which is the opposite from Si-particle/total. Thus the behaviour of Ca-salt is similar to Si-particles but not exactly same, which imply that the behaviour of calcium compounds are different from silicate dust as Ruth et al. [2007] pointed out.

The Na-salt is a particle containing Na but not Si, which is a soluble salt particle and a proxy of sea-salt. The average number ratio of Na-salt to total non-volatile particle is 28.1, 19.3, 24.5, 17.4, 16.9, and 14.8% in Holocene, YD, BA, LGM, DO-w, and DO-c, respectively. The ratio of Na-salt/total is higher in warmer stages than in colder stages.

Figure 3.5.1e shows the time series fraction of the soluble particles. In general, the contribution of Ca-salt is higher than that of Na-salt in glacial period, and vice versa in interglacial period. Number fractions of particles in each 7 climatic stage are shown in Figure 3.5.1f–l. The 7 climatic stages can be sorted into three groups; Interglacial-group (Holocene and SDS), BA (medium stage between interglacial-group and glacial group in terms of the temperature), and Glacial-group (YD, LGM, DO-w and DO-c). In the Interglacial-group, Na-salt account for about 50% of total soluble particles (48.9 % for the Holocene and 54.1 % for the SDS), whereas the Ca-salt account for more than 50% of total soluble particles in the Glacial-group (59.6 % for the YD, 57.7% for the LGM, 59.1 for the DO-w, and 60.4 % for the DO-c). In contrast to the Interglacial and the Glacial-group, the BA record shows a number ratio of CaSO_4 :NaCl close to 1. Detailed compositions in the each climatic stage are described in the next sections.



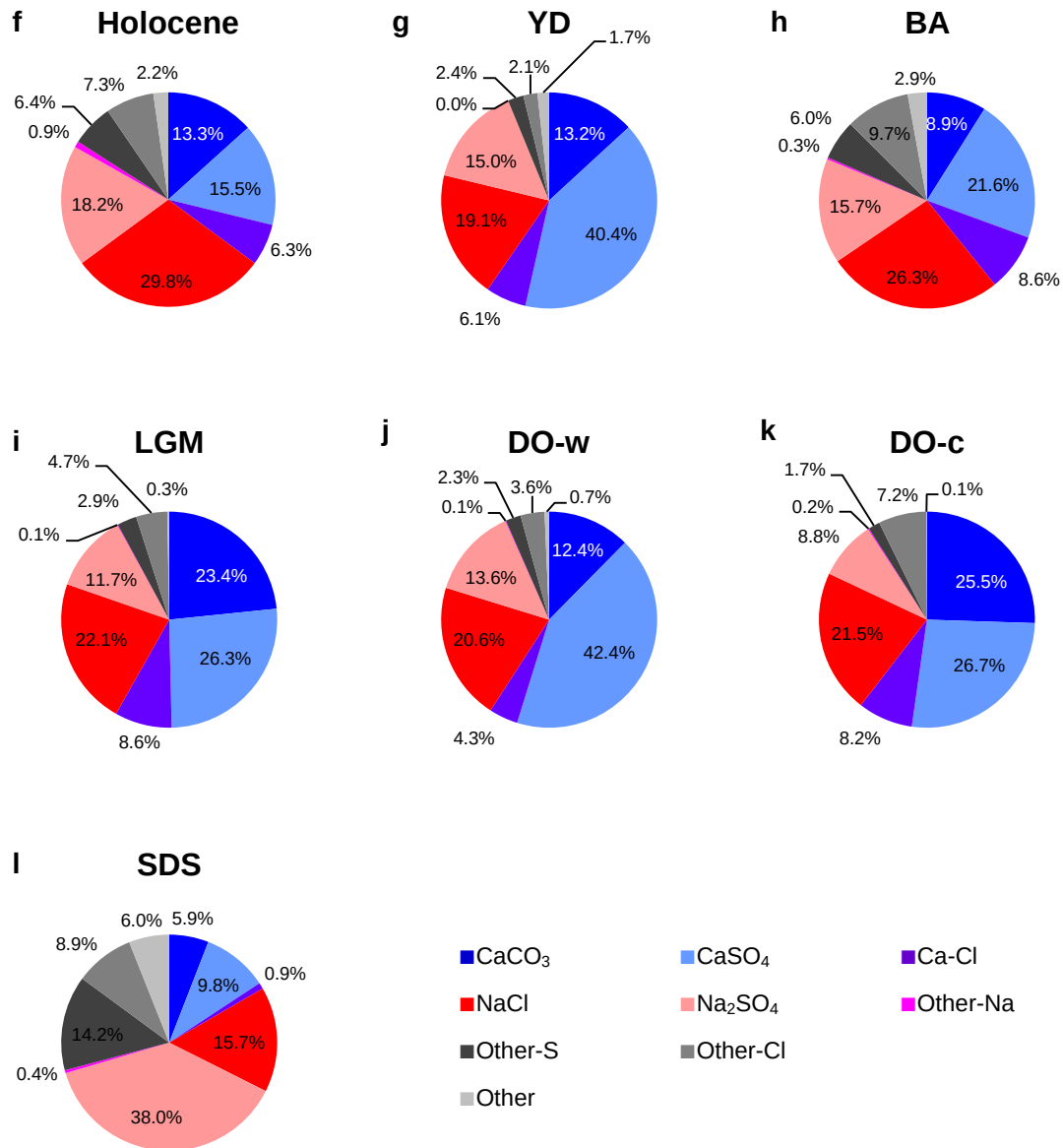


Figure 3.5.1 Time series records of the number ratio for the last 140 kyr BP at NEEM. (a) $\delta^{18}\text{O}$ profile of the NGRIP ice core (0–119.1 kyr BP) [Rasmussen et al., 2014] and δD profile of the NEEM ice core (119.1 kyr BP ~) [Dahl et al., 2013]. Measured points are plotted (Green dots). (b) Si containing particle (silicate dust) to total non-volatile particles. (c) Time-series number fraction of Ca-salt to total non-volatile particles. (d) Time-series number fraction of Na-salt to total non-volatile particles. (e) Time-series number fraction of soluble components of the NEEM ice core. (f)–(l) Number fraction of soluble components in each 7 climatic stage. Ca-Cl indicates particles containing Ca and Cl. Other-Na indicates particles containing Na but not Si, S or Cl. Other-S indicates sulfate salts other than Na₂SO₄ and CaSO₄. Other-Cl indicates chloride salts other than NaCl and Ca-Cl particles. ‘Other’ indicates soluble salts other than sulfate and chloride salts. Gray shades indicates Younger Dryas, LGM, and glacial stadials.

3.5.2 The Glacial-group (the YD, LGM, Do-w and DO-c)

The Ca-salts fraction in the Glacial-group of YD, LGM, GI and GS is higher than in the Holocene, BA, and SDS. Moreover, the Glacial-group can be divided further into two types in terms of fractions of the CaCO_3 and CaSO_4 ; cold-type (LGM and DO-c) and mild-type (YD and DO-w). The number fraction of CaSO_4 accounts for more than half of total Ca-salts in the mild-type (Figure 3.5.1e, h). In the cold-type, the fraction of CaSO_4 to Ca-salts is lower than that of the mild-type, and the fraction of CaSO_4 is almost the same as that of CaCO_3 (Figure 3.5.1g, i). Thus the major component of Ca-salt in the mild-type is CaSO_4 , and that in the cold-group is CaSO_4 and CaCO_3 .

3.5.3 The Bølling-Allerød (Medium stage between the Interglacial-group and the Glacial group)

In the BA, the number fraction of Ca-salts (other-Ca+ CaSO_4 + CaCl_2) is 39.1%, whereas that of Na-salts (other-Na+ Na_2SO_4 +NaCl) is 42.3%, thus the number ratio of Ca-salt to Na-salt close to 1, which is different from the other groups (Figure 3.5.1).

3.5.2 The Interglacial-group (the Holocene and the SDS)

The Interglacial-group of the Holocene and the SDS has larger fractions of Na-salts compared to the Glacial-group. In the Holocene stage, the fraction of Na-salt is 1.5 times larger than that of Ca-salt. This is probably because reduction rate of the sea-salt from glacial period to the Holocene is smaller than that of the terrestrial materials. According to the ion concentrations of the GRIP ice core, in inland Greenland [De Angelis et al., 1997], the concentration ratio of $\text{Na}^+/\text{Ca}^{2+}$ is significantly higher than 1 only for the Holocene.

The most abundant sulfate salt in the NEEM ice core over the last 130 kyr is CaSO_4 , but in the Holocene, Na_2SO_4 is dominating (Figure 3.2.4 and 3.5.2). The Na_2SO_4 account 9.4% of all particles, whereas it accounts for 13.0% of the all Holocene particles. The CaSO_4 accounts for 19.8% of all particles but for 11.7% of the all Holocene particles.

The fractions of Si-S- and S-particles that do not have any Na, Ca, Mg or K (sulfate salt without Na, Ca, Mg and K) in the Holocene are larger than those of all particles (Figure 3.2.4 and 3.5.2). The sulfate salt without Na, Ca, Mg and K accounts for 1.6% of all particles and for 2.8% of Holocene particles. This sulfate salt can be assumed to be $(\text{NH}_4)_2\text{SO}_4$ one of the most common sulfate salts at

present [Willison et al., 1989]. $(\text{NH}_4)_2\text{SO}_4$ arise from the neutralization of SO_4^{2-} by NH_4^+ [Warneck, 1999; Fuhrer et al., 1996], and since NH_4^+ is a major cation in the Holocene, it is not surprising that the $(\text{NH}_4)_2\text{SO}_4$ fraction has increased ub the Holocene.

7 data points of the SDS group include the Penultimate Glacial Maximum (PGM), the Last Interglacial Period (LIG), and the inception. Excluding 2 data points of the PGM (2466.20 and 2471.70 m), δD is above -288% , which is the same or higher level as in the Holocene. By focusing on the elemental combination of sulfate and chloride salts, I examined the distribution of the particles of the SDS group (Figure 3.5.3). 3 data of the inception (2314.40, 2285.80, and 2213.20 m) are similar to the average of the Greenland. The abundant combination of other-particle is Ca, that of sulfate is Ca and that of chloride is Na. Thus, the major soluble salts in the inception are other-Ca, CaSO_4 and NaCl. On the other hand, for the 2 data of the LIG (2389.20 and 2401.30 m) and 2 data of the PGM (2466.20 and 2471.70 m), the abundant combination of other-particle is K and that of sulfate is Na. Different from the inception, NaCl and CaSO_4 are rarely found. Thus, the major soluble salt in the LIG and the PGM is Na_2SO_4 , which is similar to the Antarctic Holocene composition.

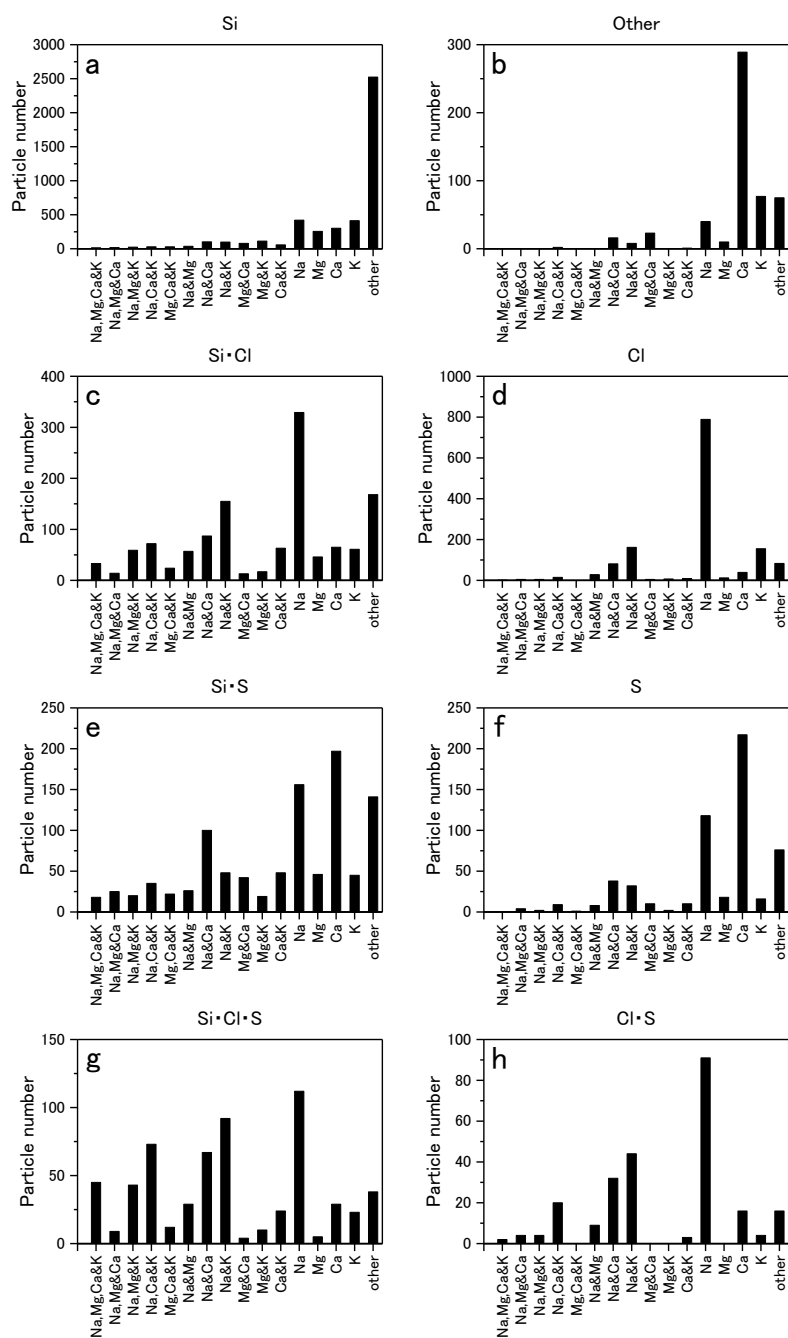


Figure 3.5.2 Same as Figure 3.2.4 except that is shown the only Holocene (NEEM).

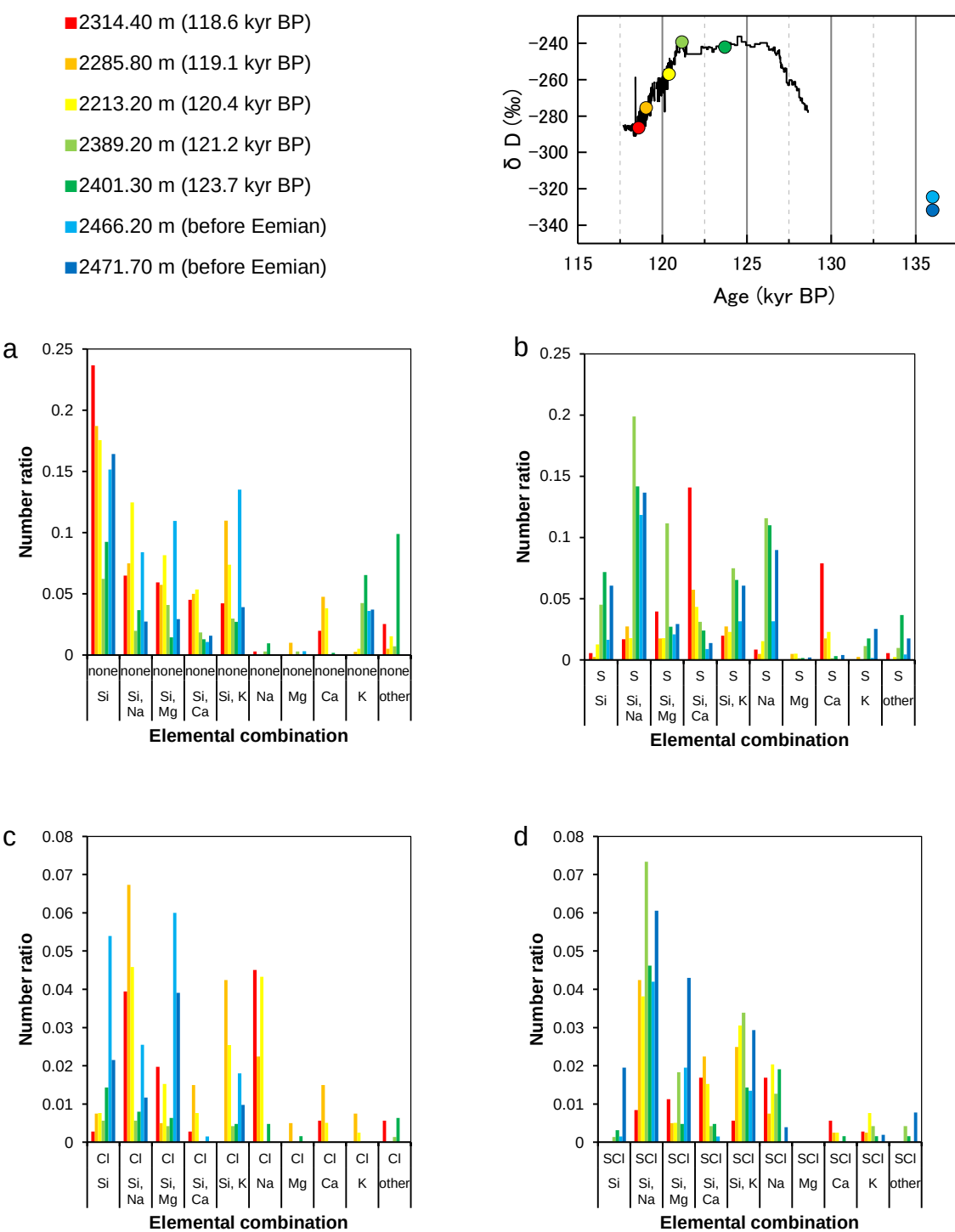


Figure 3.5.3 Distribution of the stratigraphic disruptions section particles of the NEEM ice core. The ratios are obtained by the each number of categories divided by the total particle number of each sample. **(a)** Particles without S and Cl. **(b)** Particles having S but not Cl. **(c)** Particles having Cl but not S. **(d)** Particles having both S and Cl.

CHAPTER 4

4 Seasonal variability of soluble salts in inland Antarctica and Greenland

The compositions of atmospheric aerosols have seasonal variations. The seasonal difference of the chemical compositions of particles preserved in the ice cores is important to better understand the long time scale records. To understand seasonal difference of the chemical compositions of soluble salt particles, all the year round atmospheric aerosols of present Antarctica and the NEEM ice core of the Holocene and the LGM sections were examined. The section 4.1 discusses the chemical compositions of summer and winter sea-salt aerosol in present Antarctica. The section 4.2 discusses the seasonal variability of the soluble salt particles in the Holocene and the LGM section of the NEEM ice core.

4.1 Seasonal variability of sea-salt aerosols in present inland Antarctica

It has been known that Na^+ and nssSO_4^{2-} of present Antarctic atmosphere have clear seasonal cycle. The Na^+ originated from sea-salt emission has peak in winter, whereas nssSO_4^{2-} originated from DMS emission from marine biogenic activity has peak in summer [e.g., Hara et al., 2004; Preunkert et al., 2008; Udisti et al., 2012]. It is considered that Na^+ emitted from Southern Ocean initially forms NaCl, which is sulfatized to Na_2SO_4 during its transportation. In the previous study of ionic balance of inland Antarctic ice cores predicted that most of Na^+ in Holocene forms Na_2SO_4 because ionic balance shows $[\text{SO}_4^{2-}] > [\text{Na}^+]$ and there is strong correlation between SO_4^{2-} and Na^+ [e.g., Iizuka et al., 2004]. However, there is possibility that some of winter sea-salt does not encounter the summer marine biogenic sulfate. In fact, a certain amount of NaCl was found in Holocene ice (see Chapter 3). To make clear if NaCl survived in one year, Na_2SO_4 and NaCl concentrations were calculated using the monthly concentrations of Na^+ and SO_4^{2-} by assuming that the chemical reaction of $2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ occurred completely within each single month.

The Na^+ and SO_4^{2-} concentrations were measured at Dome C in 2007 [Preunkert et al., 2008]. Concentrations of Na^+ and SO_4^{2-} are from Preunkert et al. 2008, and the calculated concentrations of

Na_2SO_4 and NaCl are shown in Figure 4.1a and 4.1b. Preunkert et al. [2008] determined 4 months for summer (Dec–Mar) and 8 months for winter (Apr–Nov). In Dec–Mar, the average concentration of Na^+ is 0.17 neq/m^3 and that of nssSO_4^{2-} is 1.07 neq/m^3 (SO_4^{2-} is 1.12 neq/m^3). In Apr–Nov, the average concentration of Na^+ is 0.34 neq/m^3 and that of nssSO_4^{2-} is 0.24 neq/m^3 (SO_4^{2-} is 0.32 neq/m^3). Calculation is as following; $[\text{Na}_2\text{SO}_4]$ equals smaller $[\text{Na}^+]$ or $[\text{SO}_4^{2-}]$, and the remaining of $[\text{Na}^+]$ equals $[\text{NaCl}]$ if $[\text{Na}^+] > [\text{SO}_4^{2-}]$. As a result, the average concentration of Na_2SO_4 in Dec–Mar is 0.17 neq/m^3 and that of NaCl is 0 neq/m^3 . In Apr–Nov, the average concentration of Na_2SO_4 is 0.24 neq/m^3 and that of NaCl is 0.09 neq/m^3 . Thus, if seasonal changes are taken into account, the NaCl exists with the molar equivalent ratio of NaCl to Na^+ of 0.23. Namely, 23% of Na^+ is expected to be NaCl , and rest of Na^+ is expected to be Na_2SO_4 through a year according to the Dome C aerosols in 2007. This result implies that several amount of NaCl precipitate on the inland Antarctic ice sheet. However, the ratio must be different by place to place, and by year to year, so further study is needed.

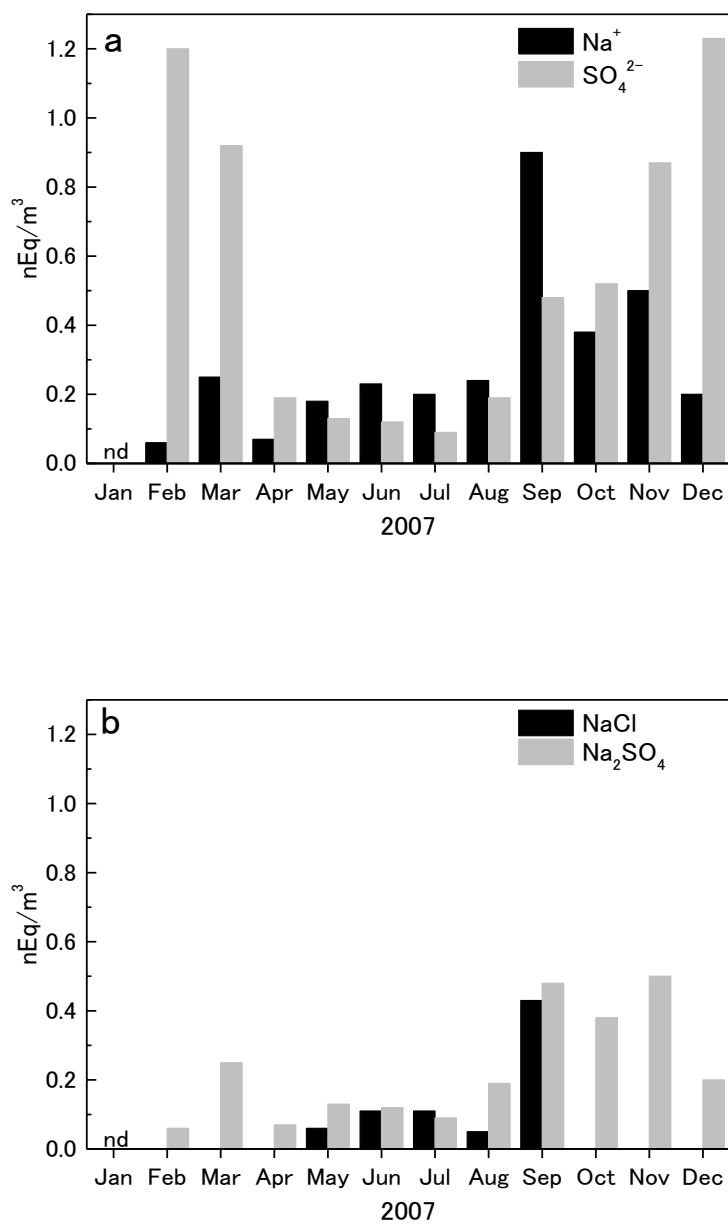


Figure 4.1 Monthly mean concentrations of ions and deduced salts. **(a)** The Na^+ and SO_4^{2-} concentrations of aerosols corrected at Dome C in 2007 [Preunkert et al., 2008]. **(b)** Deduced Na_2SO_4 and NaCl concentrations are calculated from ion concentrations of Preunkert et al., [2008].

4.2 High-resolution analysis on the NEEM ice core

Accumulation rates of the Greenland ice sheet are much higher than those of inland Antarctic ice sheet. Due to this high accumulation rates, annual layers remained. The seasonal variations can be read from the proxies such as stable water isotope and ion concentrations records [e.g., Svensson et al., 2005]. Since atmospheric aerosol composition in the present is affected by the anthropogenic emission, today's seasonal variability of aerosol composition cannot be a reference for the aerosol composition in the preindustrial era. To understand the chemical compositions of seasonal variability in the preindustrial era including not only warm periods but also glacial period, the layer analysis was carried out on the Holocene and LGM sections of the NEEM ice core.

4.2.1 Characteristics of the concentrations of impurities in the glacial and present ice

All Greenland ice cores reaching into glacial ice have been reported to reveal bands of cloudy and clear ice [e.g., Meese et al., 1997; Shimohara et al., 2003]. In particular, the occurrence of cloudy bands in glacial ice with high concentrations of dust and other impurities has long been recognized [e.g., Ram and Koenig, 1997; Svensson et al., 2005]. From visual observation, 5 layers of 1 cm thickness were selected from the LGM section. LGM-01, LGM-03, and LGM-05 are from clear layers (1560.00, 1556.17, and 1556.25 m), and LGM-02 and LGM-04 (1556.13 and 1556.22 m) are from cloudy bands with high dust and Ca^{2+} concentrations (Figure 4.2.1a).

On the other hand for the interglacial ice, clear layers and cloudy bands are not as prominent due to the much lower impurity content. However, ion and dust concentrations show clear seasonal variability [Rasmussen et al., 2006], so the seasonality can be determined from their concentrations. At present, it is known that dust and Ca^{2+} are of terrestrial origin and peak in spring [e.g., Whitlow et al., 1992; Kuramoto et al., 2011]. The Na^+ originate from sea-salt and has a peak in winter, and NO_3^- and NH_4^+ that originate mainly from bacterial decomposition in soils, peak in the summer [Whitlow et al., 1992; Fuhrer et al., 1996; Kuramoto et al., 2011]. Apart from volcanism, the natural source of SO_4^{2-} is mainly from DMS emission from marine biogenic activity and continental biogenic emissions that peaks in summer [Kuramoto et al., 2011]. I assume that Holocene-01 is considered to be winter (Na^+ peak), Holocene-02 and Holocene-04 are considered to be summer (NH_4^+ and NO_3^- peak), and Holocene-03 is considered to be spring (dust and Ca^{2+} peak) (Figure 4.2.2a). Detailed sample information is described in Chapter 2 (Table 2.4).

4.2.2 Characteristics of the particle compositions in the LGM section

The dust concentrations shows clear differences between cloudy bands and clear layers, on the other hand, more than 90% of the particles contain Si in all layers (Figure 4.2.1b–f), thus the LGM section is characterized by a high mineral dust fraction. This result shows that even in layers with low dust concentrations (clear layer), the fraction of mineral dust is high.

For the soluble components, Ca-salts accounts more than 80% of the soluble components in the cloudy bands (LGM-02 and 04) (Figure 4.2.1h and j). The Ca-salts consists of CaCO_3 and CaSO_4 in the ratio 1:1. The fraction of Na-salts is less than 10%, and most of it is in the form of Na_2SO_4 . The soluble components in the cloudy bands therefore mainly consist of terrestrial materials. In contrast, clear layers have more Na-salts (LGM-01, 03 and 05) (Figure 4.2.1g and k).

The Na-salts consists of NaCl and Na_2SO_4 , and more than 60% of the Na-salt is in the form of NaCl . Therefore, the contribution of sea-salt to soluble components is higher in clear layers than in cloudy bands. The soluble components shows clear differences between cloudy bands and clear layers even though both, cloudy bands and clear layers have more than 90% of Si (dust) in the non-volatile particles

4.2.3 Characteristics of the particle compositions in the Holocene section

The particle compositions show clear seasonality in the Holocene section. 75% of the particles of Holocene-01 and 03 (winter and spring) contain Si, whereas Si containing particles of Holocene-02 and 04 (summer) account for less than 60% of the particles (Figure 4.2.2b–e). This suggests that the fraction of dust to non-volatile particles in winter and spring layers is higher than that of summer layer. Comparing the Holocene section to the LGM section, even in spring (dust season), the fraction of Si containing particle is lower than LGM clear layer. This result suggests that atmosphere in LGM has larger proportion of silicate mineral than that in Holocene dust season.

For the composition of soluble components, the fraction of Holocene Na-salts in winter (Figure 4.2.2f) is larger than that of summer (Figure 4.2.2g) and spring (Figure 4.2.2h). Moreover, the fraction of NaCl is larger than that of Na_2SO_4 , showing that the NaCl fraction is high in winter layer. A high Na-salts fraction with high NaCl content suggest that the sulfatization of NaCl was not enhanced in winter probably due to an increasing sea-salt (NaCl) emission and decreasing DMS (SO_4^{2-}) emission. The fraction of Holocene Ca-salts in spring (Figure 4.2.2h) is larger than that of winter (Figure 4.2.2f)

and summer (Figure 4.2.2g). This result indicates that the contribution of terrestrial material is high in spring layers. The CaSO_4 fraction is high in this layer. The high CaSO_4 fraction in spring layer suggests that large amount of Ca^{2+} , which mainly originates from Asian deserts [e.g., Svensson et al., 2000; Bory et al., 2003], was sulfatized during the long-range transportation. Holocene-02 seems to represent summer aerosols (Figure 4.2.2g). In this sample, the fraction of “other-salt” (other-S + other-Cl + the other salt) is larger than in that of winter (Figure 4.2.2f) and spring (Figure 4.2.2h). Especially, the fraction of other-sulfate is high. This other-sulfate can be assumed to be $(\text{NH}_4)_2\text{SO}_4$. Both NH_4^+ and SO_4^{2-} peak in summer [Kuramoto et al., 2011], so it is reasonable to consider that NH_4^+ and SO_4^{2-} form $(\text{NH}_4)_2\text{SO}_4$ in the summer.

There may be almost no NaCl in summer in inland Antarctica, in contrast, the NaCl remained even in summer in Greenland. For instance, Holocene-04 which is considered to be summer layer has high NaCl fraction. The fraction of NaCl is probably different from year to year, but a certain amount of NaCl may remain without being sulfatization. Also, a certain amount of CaCO_3 was found in all layers.

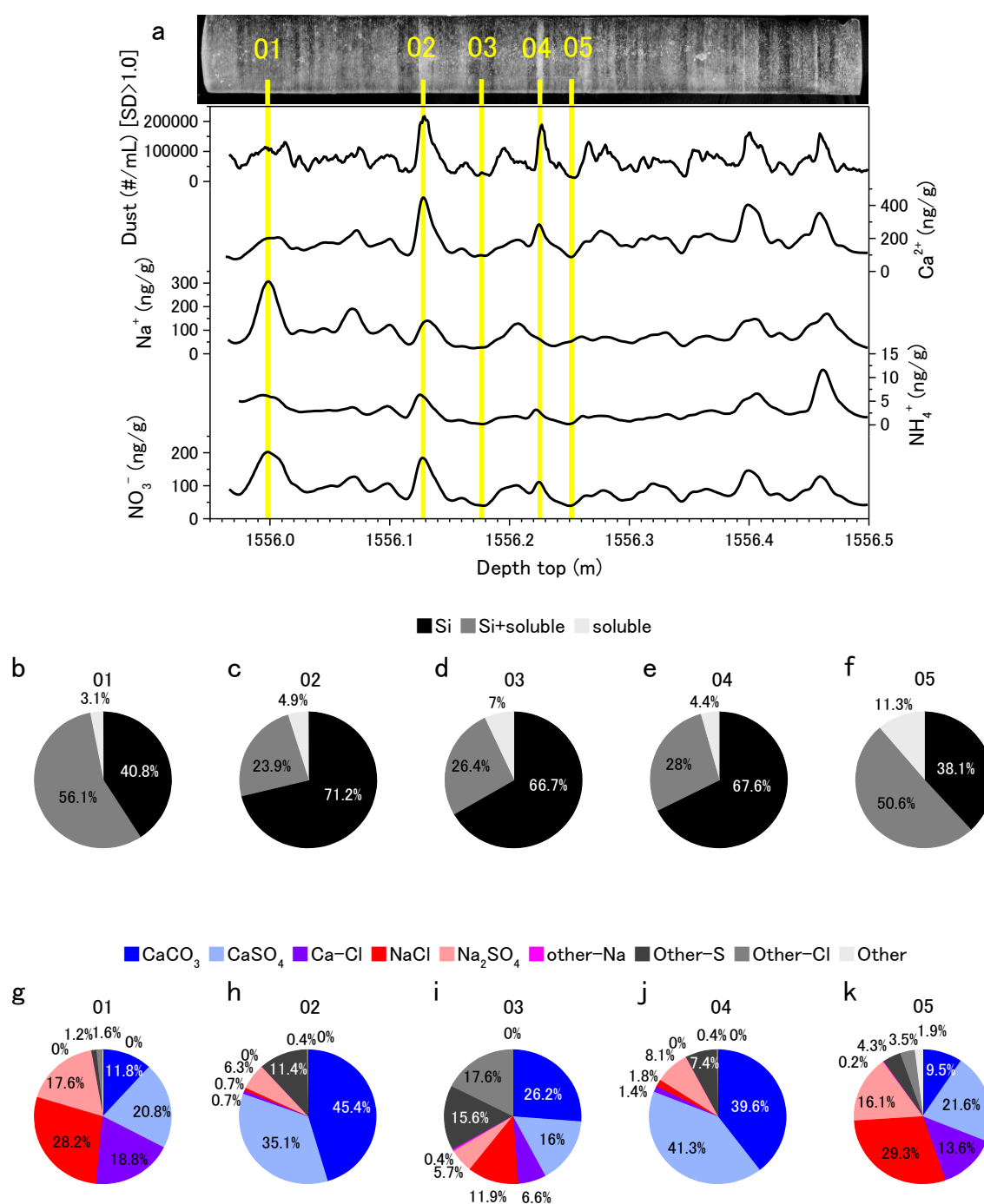


Figure 4.2.1 High-resolution analysis of the LGM section of the NEEM ice core. **(a)** Dust, Ca^{2+} , Na^+ , NH_4^+ , and NO_3^- concentrations. **(b)** to **(f)** Number fraction of soluble and insoluble particles of subsamples 01-05. “Si” indicates particles containing Si but not S or Cl (insoluble). “Si+soluble” indicates particles containing Si, S and/or Cl. This particle is mixture of insoluble and soluble particles. “Soluble” indicates particles without Si (soluble). **(g)** to **(k)** Number fraction of soluble salts of 01-05. Ca-Cl indicates particles containing Ca and Cl. Other-Na indicates particles containing Na but not Si, S or Cl. Other-S indicates sulfate salts other than Na_2SO_4 and CaSO_4 . Other-Cl indicates chloride salts other than NaCl and Ca-Cl particles. ‘Other’ indicates soluble salts other than sulfate and chloride salts. Gray shades indicates Younger Dryas, LGM, and glacial stadials.

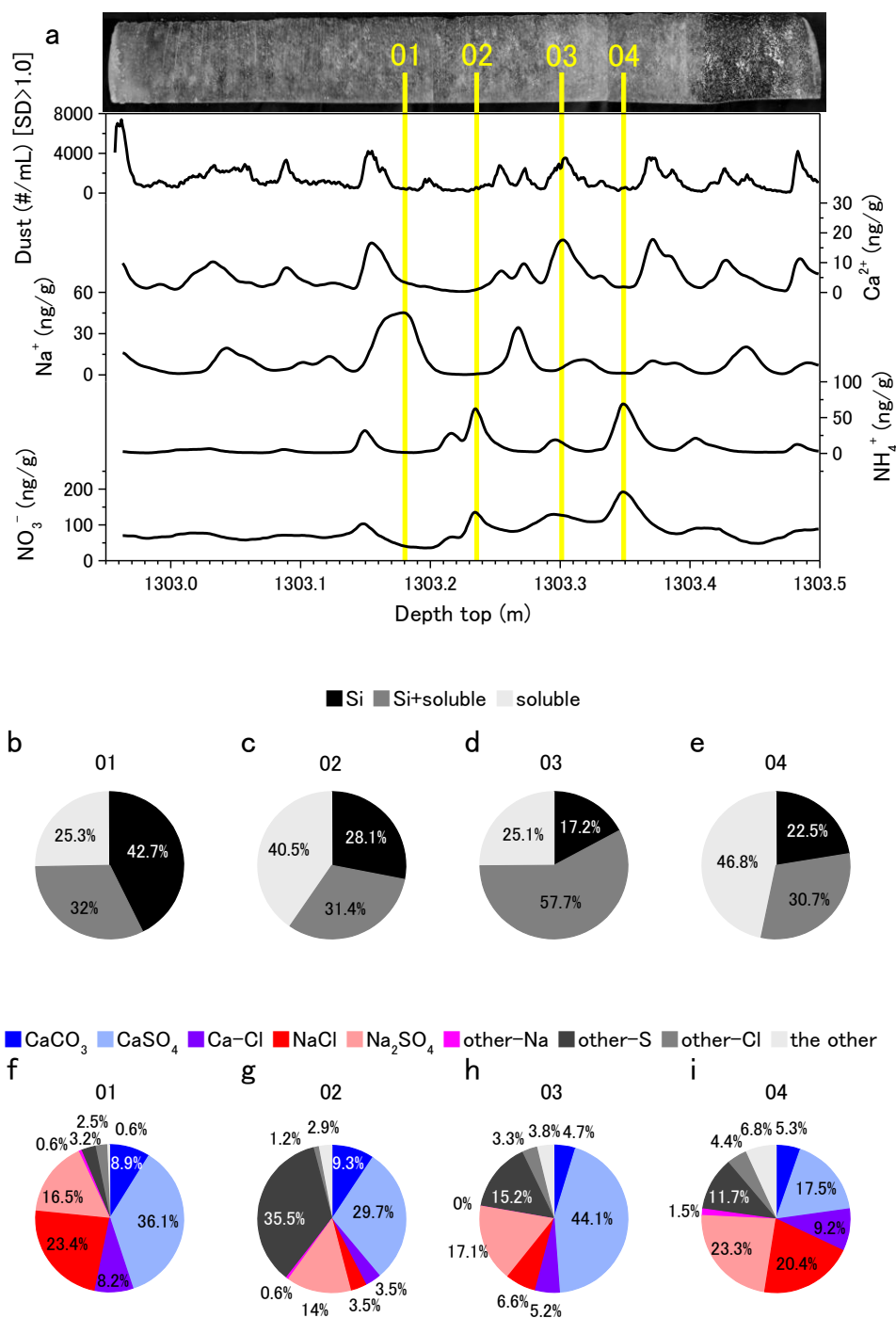


Figure 4.2.2 High resolution analysis of the Holocene section. See figure 4.2.1 for captions.

CHAPTER 5

5 Time series variations of soluble salts during the last termination in Antarctica and Greenland

This chapter discusses time series variations of soluble salts in Antarctica and Greenland by focusing on the last termination.

5.1 Mass fractions of Ca-salt and Na-salt in the Dome Fuji, Dome C and NEEM ice cores

The number fractions of particle compositions and their time series variations of the Dome Fuji, Dome C and NEEM ice cores were shown in Chapter 3. This section describes the mass fractions of Ca-salt and Na-salt in Dome Fuji, Dome C and NEEM ice. The Ca^{2+} and Na^+ are the major cations in Dome Fuji, Dome C, and NEEM. The anions are probably preserved as both acids and salts in the ice core (e.g., SO_4^{2-} can be exist as sulfate-salt and sulfuric acid), whereas the cations are present as soluble salts in the ice core. Thus, the considering the Ca-salt and Na-salt means covering most of soluble salts in the ice cores.

5.1.1 The Dome Fuji ice core

Figure 5.1.1a shows the mass fractions of Ca-salt and Na-salt from 25.0 to 9.6 kyr BP at Dome Fuji. As shown in Chapter 3, the major soluble salts are CaSO_4 , Na_2SO_4 , and NaCl during this period. The period from 25.0 to 18.0 kyr BP (LGM) is characterized by the high CaSO_4 and NaCl , and low Na_2SO_4 fractions (Figure 5.1.1a). Between 18.0 and 16.0 kyr BP, fraction of CaSO_4 and NaCl decreased and that of Na_2SO_4 increased. The period from 16.0 to 11.7 kyr BP is characterized by the low CaSO_4 and NaCl , and high Na_2SO_4 fractions. The average fractions during these periods are written in Table 5.1.

Focusing on the CaSO_4 and Na_2SO_4 of the major sulfate salts, the ratio of Na_2SO_4 to CaSO_4 starts low at 0.60 ± 0.67 during 25.0–18.0 kyr BP, increases between 18.0 and 16.0 kyr BP, and then stays

high at 4.70 ± 2.61 through 11.7 kyr BP (Figure 5.1.1b). At 16.8 kyr BP, the ratio changes from below 1 ($\text{CaSO}_4 > \text{Na}_2\text{SO}_4$) to above 1 ($\text{CaSO}_4 < \text{Na}_2\text{SO}_4$), showing the same trend as that found previously for the number ratio in Chapter 3 (Figure 3.4.1). This result indicates that the primary sulfate salt changes from CaSO_4 to Na_2SO_4 at 16.8 kyr BP. After 11.0 kyr BP, the ratio shows sometimes very low. The ratios show below 1 (0.04–0.43) at 9.8, 10.0, 10.1, and 10.7 kyr BP.

Focusing on the NaCl and Na_2SO_4 of the major Na-salts, the ratio of NaCl to Na_2SO_4 starts high, decreased between 17.3 and 16.3 kyr BP, and then stays low after that (Figure 5.1.1c). The NaCl/ Na_2SO_4 has high variability after 12.3 kyr BP. The average ratio for 16.0–11.7 kyr BP shows below 0.54 (Table 5.1), but at 12.3, 12.0, 11.2, 11.1, 10.1, 9.8 and 9.6 kyr BP shows a relatively high value of 0.77–5.93.

5.1.2 The Dome C ice core

Figure 5.1.2a shows the mass fraction of Ca-salt and Na-salt from 26.0–6.8 kyr BP of the Dome C ice core. As well as at Dome Fuji, the major soluble salts are CaSO_4 , Na_2SO_4 , and NaCl during this period. The period from 26.0 to 18.0 kyr BP (LGM) is characterized by the high CaSO_4 and NaCl, and low Na_2SO_4 fractions. After 18.0 kyr BP, the fraction of CaSO_4 and NaCl decreased and that of Na_2SO_4 increased. The period from 17.0 to 11.7 kyr BP is characterized by the low CaSO_4 and NaCl, and high Na_2SO_4 fractions. The average fractions during this period are written in Table 5.1.

Focusing on the CaSO_4 and Na_2SO_4 of the major sulfate salts, the ratio of Na_2SO_4 to CaSO_4 starts low at 1.46 ± 0.84 during 26.0–18.2 kyr BP (Figure 5.1.2b). After that, the ratio shows a high value of 11.12 ± 12.32 through 6.8 kyr BP. Excepting of 24.8 and 26.0 kyr BP, the ratio shows above 1. This result indicates that Na_2SO_4 concentration is always higher than CaSO_4 concentration after 24.8 kyr BP.

Focusing on the NaCl and Na_2SO_4 of the major Na-salts, the ratio is relatively higher for 26.0–18.2 kyr BP than in 16.9–6.8 kyr BP. The average ratio is 0.77 ± 0.80 for 26.0–18.2 kyr and that is 0.17 ± 0.13 in 16.9–6.8 kyr BP. The ratio after 16.9 kyr BP shows below 0.24, but at 9.5, 9.2, 8.8, 7.9, and 7.5 kyr BP shows a relatively high value of 0.37–0.46 (Figure 5.1.2c).

Table 5.1 Fractions and ratios of Ca-salt and Na-salt of the Dome Fuji and Dome C ice cores.

Fractions of Ca-salt plus Na-salt (%)									Ratios	
			CaSO ₄	Other-Ca	CaCl ₂	NaCl	Na ₂ SO ₄	Other-Na	NaCl/Na ₂ SO ₄	Na ₂ SO ₄ /CaSO ₄
DF	25.0-18.0	average	43.7	3.0	9.1	23.7	20.3	0.1	1.69	0.60
	kyr BP	SD	14.0	4.5	4.9	10.1	14.0	0.3	1.22	0.67
	16.0-11.7	average	12.1	11.2	5.8	19.9	49.2	1.8	0.54	4.70
	kyr BP	SD	5.2	11.2	8.2	12.5	17.1	2.7	0.50	2.61
DC	26.0-18.0	average	32.9	5.1	2.8	21.1	38.1	0.0	0.77	1.46
	kyr BP	SD	17.9	4.8	2.1	16.1	19.9	0.0	0.80	0.84
	17.0-11.7	average	9.5	8.4	2.9	10.0	68.4	0.1	0.15	15.18
	kyr BP	SD	6.8	8.3	4.8	5.8	9.5	0.1	0.09	16.21

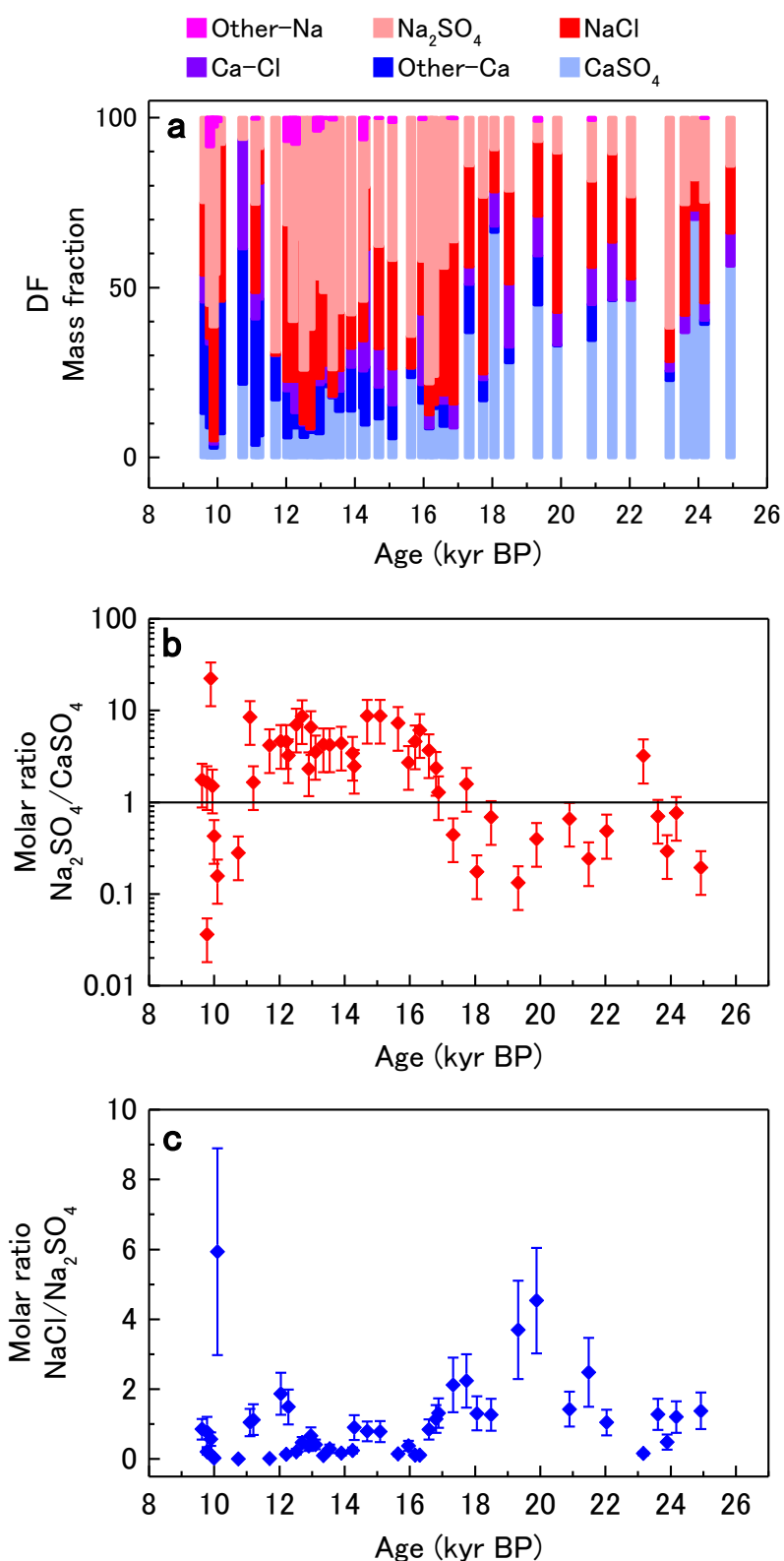


Figure 5.1.1 Time series variations of Na-salt and Ca-salt of the Dome Fuji ice core in 25.0–9.6 kyr BP. (a) Mass fraction of Ca-salt and Na-salt. (b) Molar ratio of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$. (c) Molar ratio of $\text{NaCl}/\text{Na}_2\text{SO}_4$.

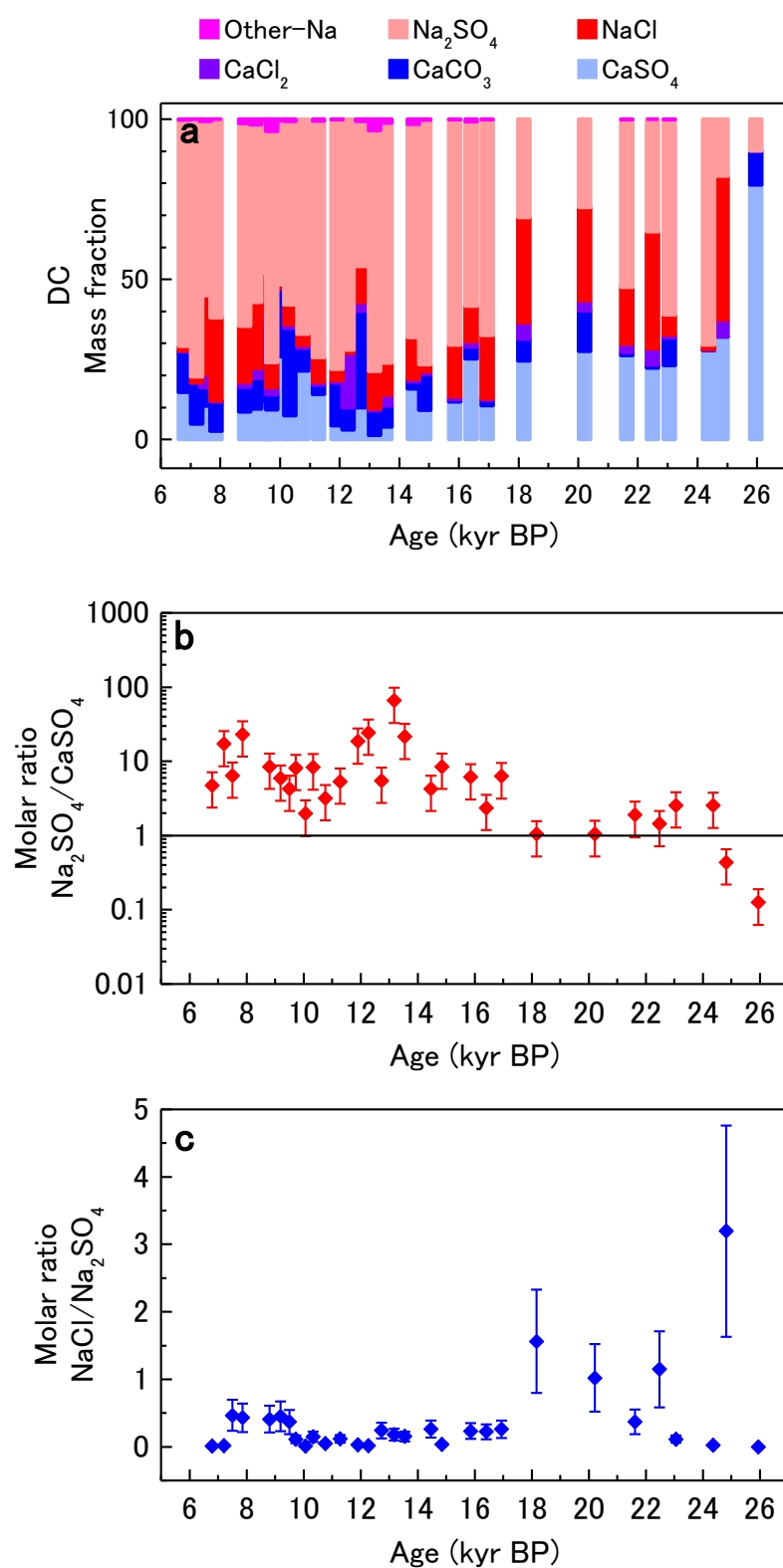


Figure 5.1.2 Time series variations of Na-salt and Ca-salt of the Dome C ice core in 26.0–6.8 kyr BP. (a) Mass fraction of Ca-salt and Na-salt. (b) Molar ratio of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$. (c) Molar ratio of $\text{NaCl}/\text{Na}_2\text{SO}_4$.

5.1.3 The NEEM ice core

Table 5.2 and Figure 5.1.3 shows the mass fraction of Ca-salt and Na-salt from 27.0–8.9 kyr BP at NEEM. As shown in Chapter 3, the major soluble salts are CaCO_3 , CaSO_4 , Na_2SO_4 , and NaCl during this period. The soluble salts composition in the Last Glacial Maximum (LGM) is characterized by the high Ca-salt with high CaCO_3 fraction. In the Bølling-Allerød (BA), CaCO_3 fraction decreased, whereas the NaCl and Na_2SO_4 fractions increased. In the Younger Dryas (YD), fractions of CaCO_3 and CaSO_4 increased, whereas those of NaCl and Na_2SO_4 decreased. In the Holocene, fractions of CaCO_3 and CaSO_4 decreased, whereas those of NaCl and Na_2SO_4 increased.

Most of the plots of the ratio of Na_2SO_4 to CaSO_4 show below 1 from 26.9 to 11.7 kyr BP. The average value in this period is 0.57 ± 0.37 . After 11.7 kyr BP, the ratio shows a high value with high variability (4.10 ± 4.77) (Figure 5.1.3b). This result indicates that the contribution of Na_2SO_4 increased in the Holocene.

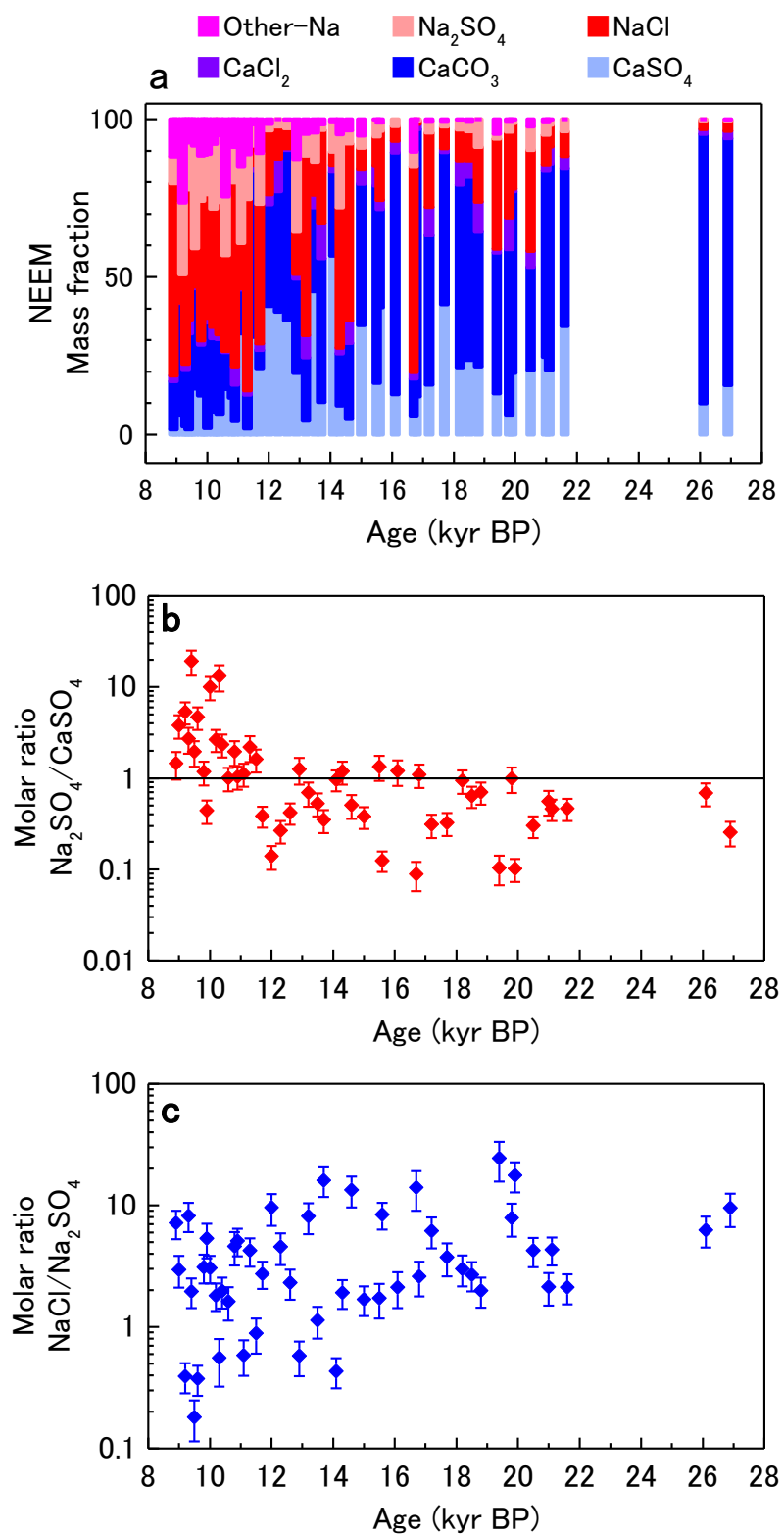
The ratio of NaCl to Na_2SO_4 shows decreasing trend from 26.9 to 8.9 kyr BP, but which has high variability (Figure 5.1.3c). This result indicates that the contribution of NaCl decreased, while that of Na_2SO_4 increased gradually.

The ratio of CaCO_3 to CaSO_4 also shows decreasing trend from 26.9 to 8.9 kyr BP (Figure 5.1.3d). Especially, the ratio after 10.2 kyr BP shows a low value (0.75 ± 0.18). This result indicates that the contribution of CaCO_3 decreased and that of CaSO_4 increased gradually.

Table 5.2 Fractions and ratios of Ca-salt and Na-salt of the NEEM ice cores

		Fractions of Ca-salt plus Na-salt (%)							
		CaSO ₄	CaCO ₃	CaCl ₂	NaCl	Na ₂ SO ₄	Other-Na	Ca-salt	Na-salt
Holocene	mean	12.7	29.8	2.9	31.5	14.3	8.9	45.3	54.7
	std. dev.	10.9	20.9	4.8	20.7	8.0	7.1	25.2	25.2
YD	mean	38.6	41.5	4.7	12.3	2.4	0.5	84.8	15.2
	std. dev.	1.9	9.2	4.1	5.9	0.3	0.6	6.3	6.3
BA	mean	21.6	27.0	5.0	30.7	11.2	4.6	53.5	46.5
	std. dev.	19.5	8.6	3.3	20.5	8.0	3.6	21.3	21.3
LGM	mean	20.6	52.0	4.1	18.1	3.9	1.3	76.7	23.3
	std. dev.	9.8	21.0	3.0	17.4	3.8	2.5	21.3	21.3

		Ratios		
		NaCl/Na ₂ SO ₄	CaCO ₃ /CaSO ₄	Na ₂ SO ₄ /CaSO ₄
Holocene	mean	2.85	5.13	2.78
	std. dev.	2.25	5.20	3.17
YD	mean	5.49	1.09	0.06
	std. dev.	3.04	0.30	0.01
BA	mean	5.96	2.56	0.95
	std. dev.	6.13	1.75	0.83
LGM	mean	6.21	3.30	0.23
	std. dev.	5.83	2.36	0.23



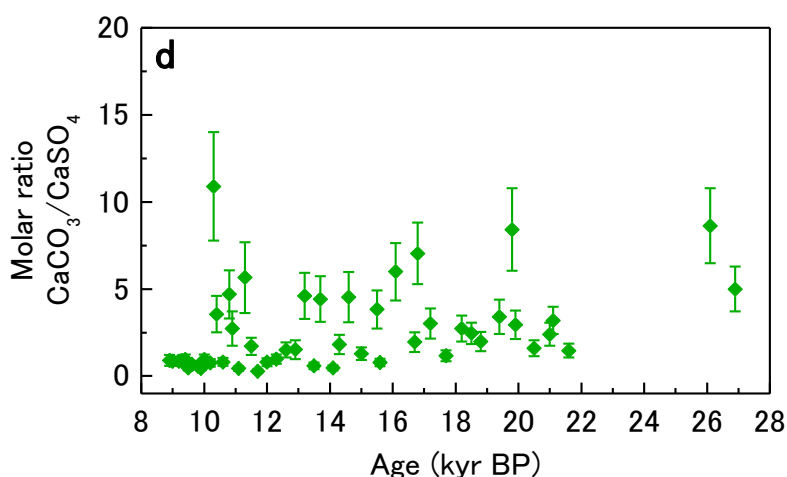


Figure 5.1.3 Time series variations of Na-salt and Ca-salt of the NEEM ice core in 26.9–8.9 kyr BP. (a) Molar fraction of Ca-salt and Na-salt. (b) Molar ratio of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$. (c) Molar ratio of $\text{NaCl}/\text{Na}_2\text{SO}_4$. (d) Molar ratio of $\text{CaCO}_3/\text{CaSO}_4$.

5.1.4 Differences between Greenland and Antarctica

In inland Antarctica, the ratio of Na-salt to Ca-salt is almost 1 in the LGM, whereas (Table 5.1) the Na-salt concentration is more than two times higher than Ca-salt concentration in the Holocene. On the other hand, in Greenland, the Ca-salt concentration is more than two times higher than Na-salt concentration in the LGM, whereas the ratio of Na-salt to Ca-salt is almost 1 in the Holocene. Thus, the contribution of sea-salt is higher in inland Antarctica, whereas the contribution of terrestrial material is higher in Greenland. In addition, the contributions of CaSO_4 and Na_2SO_4 are higher in inland Antarctica, whereas those of CaCO_3 and NaCl are higher in Greenland. The CaSO_4 is a primary aerosol, coming from terrestrial gypsum, and also a secondary aerosol, coming from neutralization of CaCO_3 by H_2SO_4 . The Na_2SO_4 is a secondary aerosol coming from neutralization of NaCl by H_2SO_4 . Therefore, the contribution of secondary aerosols is higher in inland Antarctica, whereas that of primary aerosols is higher in Greenland.

5.2 Causes of the changes in the soluble salts in Antarctic ice cores

In this section, causes of changes in the major soluble salts of NaCl, NaSO₄ and CaSO₄ over the last termination in the Antarctic ice cores are discussed.

5.2.1 First half of the last termination (25–16 kyr BP)

From 25 to 18 kyr BP, the CaSO₄ and NaCl fractions are high and the Na₂SO₄ fraction is low both at Dome Fuji and Dome C. The major source of Ca²⁺ during the LGM is Patagonia in South America (farther than the Southern Ocean) [Delmonte et al., 2004, 2008], thus the transport distance of Ca²⁺ is longer than that for sea-salt from the Southern Ocean (Na⁺). The long transport enables sulfatization of Ca²⁺ in the atmosphere more than that of Na⁺. Also, Röthlisberger et al. [2003b] suggested that Ca²⁺ forms sulfate salt prior to Na⁺. The ionic balance for 25–18 kyr BP shows [SO₄²⁻] > [Ca²⁺], but [SO₄²⁻] < [Ca²⁺] + [Na⁺] both in Dome Fuji and Dome C (Table 5.3; Figure 5.2.1). Namely, the SO₄²⁻ exceeds Ca²⁺, but not enough to sulfatize both Ca²⁺ and Na⁺ during this period. Note that the NH₄⁺ concentration for 25–16 kyr BP in the Dome Fuji ice core is around 0.1 µeq/L, which is only minor contribution compared to the Na⁺ and Ca²⁺ concentrations (Table 5.3; Figure 5.2.1). The NH₄⁺ concentration of the Dome C ice core should be similar to that of the Dome Fuji ice core, so the NH₄⁺ concentration can be ignored in this period. These results imply that most of the Ca²⁺ forms CaSO₄ but some of Na⁺ remained as NaCl due to high Ca²⁺ concentration for 25–18 kyr BP. According to Sakurai et al. [2011], the concentration of Ca²⁺ correlates strongly with the frequency of CaSO₄ particles measured by Raman spectroscopy, and suggested that most Ca²⁺ ions form CaSO₄ at every depth of the last termination.

Between 18 and 16 kyr BP, the CaSO₄ and NaCl fractions decreased and the Na₂SO₄ fraction increased both in the Dome Fuji and Dome C ice cores. This change is probably due to a dramatic decrease in Ca²⁺ (Figure 5.2.2). In this period, the Ca²⁺ concentration decreased by a factor more than 5 at both sites, whereas the Na⁺ concentration decreased by a factor less than 2 at both sites. In the Dome Fuji ice core around 17 kyr BP, the ionic balance shows [SO₄²⁻] < [Na⁺] + [Ca²⁺] and [SO₄²⁻] ≅ 2[Ca²⁺]. If all SO₄²⁻ forms CaSO₄ and Na₂SO₄, it can be assumed that [CaSO₄] ≅ [Na₂SO₄]. As I showed in section 5.1.1 (figure 5.1.1), the molar ratio of Na₂SO₄/CaSO₄ was near to 1 around 17 kyr BP. This correspondence indicates that the ionic balance can explain why the Na₂SO₄/CaSO₄ ratio of the sublimation results show values near to 1 around 17 kyr BP.

5.2.2 Latter half of the last termination (16–11.7 kyr BP), and Holocene (11.7 kyr BP~)

In the latter half of the last termination (16–11.7 kyr BP), the CaSO_4 and NaCl fractions are low and the Na_2SO_4 fraction is high. In this period, Patagonian glaciers receded and the vegetation-covered area increased as a result of the warming [Siani et al., 2010; Sagredo et al., 2011], which suppresses the dust and with it the Ca^{2+} emission [Kaiser and Lamy, 2010]. In the Southern Ocean, due to the increasing sea surface temperature, the sea-ice area reduced which lead to decrease sea-salt (Na^+) emissions [Röthlisberger et al., 2003a; Lamy et al., 2007; Röthlisberger et al., 2008; Kaiser and Lamy, 2010] (Figure 5.2.2). The contribution of the NH_4^+ concentration for 16–11.7 kyr BP increased, but the sum of $[\text{Ca}^{2+}]$, $[\text{Na}^+]$ and $[\text{NH}_4^+]$ is smaller than $[\text{SO}_4^{2-}]$ ($[\text{SO}_4^{2-}] > [\text{Ca}^{2+}] + [\text{Na}^+] + [\text{NH}_4^+]$) in the Dome Fuji ice core (Table 5.3; Figure 5.2.1). The ionic balance of the Dome C ice core should be similar to that of the Dome Fuji ice core. In addition, the Ca^{2+} and NH_4^+ concentrations are very low, so the Na^+ is dominant. For the case of Dome Fuji, the Na^+ concentration is more than 6 times larger than the Ca^{2+} concentration. If all Ca^{2+} and Na^+ are in the form of CaSO_4 and Na_2SO_4 , it can be assumed that $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ ratio is close to 6, and $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratio is close to 0. The $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ and $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratios of the sublimation results are 4.70 ± 2.61 and 0.54 ± 0.50 , respectively (Table 5.1). These results imply that the cause of changes in the salts compositions in the latter half of the last termination is different reduction rates of Ca^{2+} and Na^+ concentrations.

From the above discussion, changes in the salt compositions seem to be explained roughly by the ionic balance. However, between 12.3 and 9.6 kyr BP in Dome Fuji, and between 9.5 and 7.5 kyr BP in Dome C, the $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratio shows high values (Figure 5.1.1c, 5.1.2c). These high ratios cannot be explained by the ionic balance, because the ionic balance is $[\text{SO}_4^{2-}] > [\text{Na}^+] + [\text{Ca}^{2+}]$ both in Dome Fuji and Dome C after 12.3 kyr BP, so all of the Na^+ and Ca^{2+} should be in the form of Na_2SO_4 and CaSO_4 according to the ionic balance. This high $\text{NaCl}/\text{Na}_2\text{SO}_4$ variability is likely linked to an increase in the seasonal contribution of NaCl to the atmospheric aerosol in winter during the period (see Chapter 4).

Table 5.3 Ion concentrations in Antarctic ice cores ($\mu\text{eq/L}$).

			Ca^{2+}	Na^+	SO_4^{2-}	NH_4^+
DF	11.7–16.0 kyr BP	mean	0.23	1.38	2.21	0.25
		std. dev.	0.13	0.51	0.49	0.31
	16.0–18.0 kyr BP	mean	1.26	2.84	3.25	0.10
		std. dev.	0.66	0.59	0.70	0.19
	18.0–25.0 kyr BP	mean	2.90	4.43	4.52	0.15
		std. dev.	0.76	0.72	0.73	0.32
DC	11.7–16.0 kyr BP	mean	0.19	1.56	2.33	
		std. dev.	0.10	0.40	0.31	
	16.0–18.0 kyr BP	mean	1.25	3.40	3.73	
		std. dev.	0.53	0.71	0.60	
	18.0–26.0 kyr BP	mean	2.37	4.39	4.39	
		std. dev.	0.45	0.28	0.45	

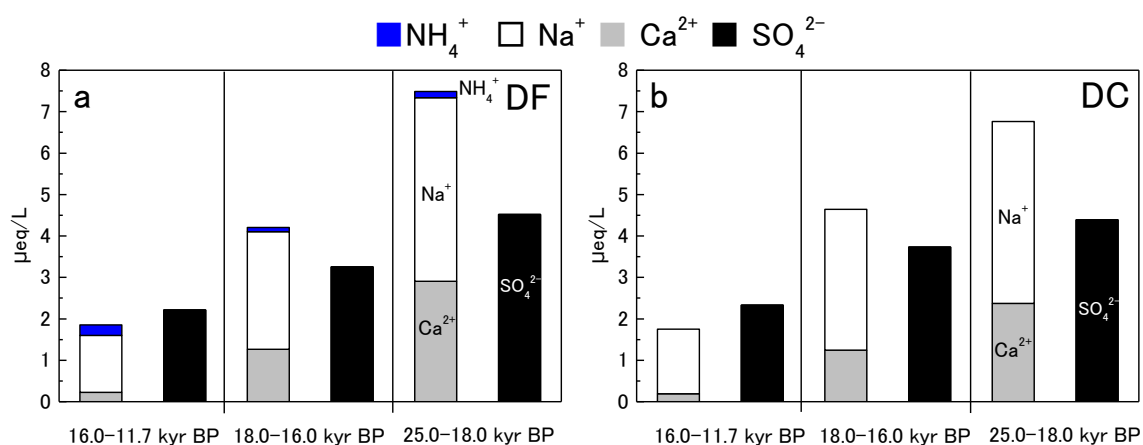


Figure 5.2.1 Ionic balance of the Na^+ , Ca^{2+} and SO_4^{2-} in 25.0–18.0 kyr BP, 18.0–16.0 kyr BP and 16.0–11.7 kyr BP. (a) Dome Fuji. (b) Dome C. There is no available data of the NH_4^+ concentration of the Dome C ice core.

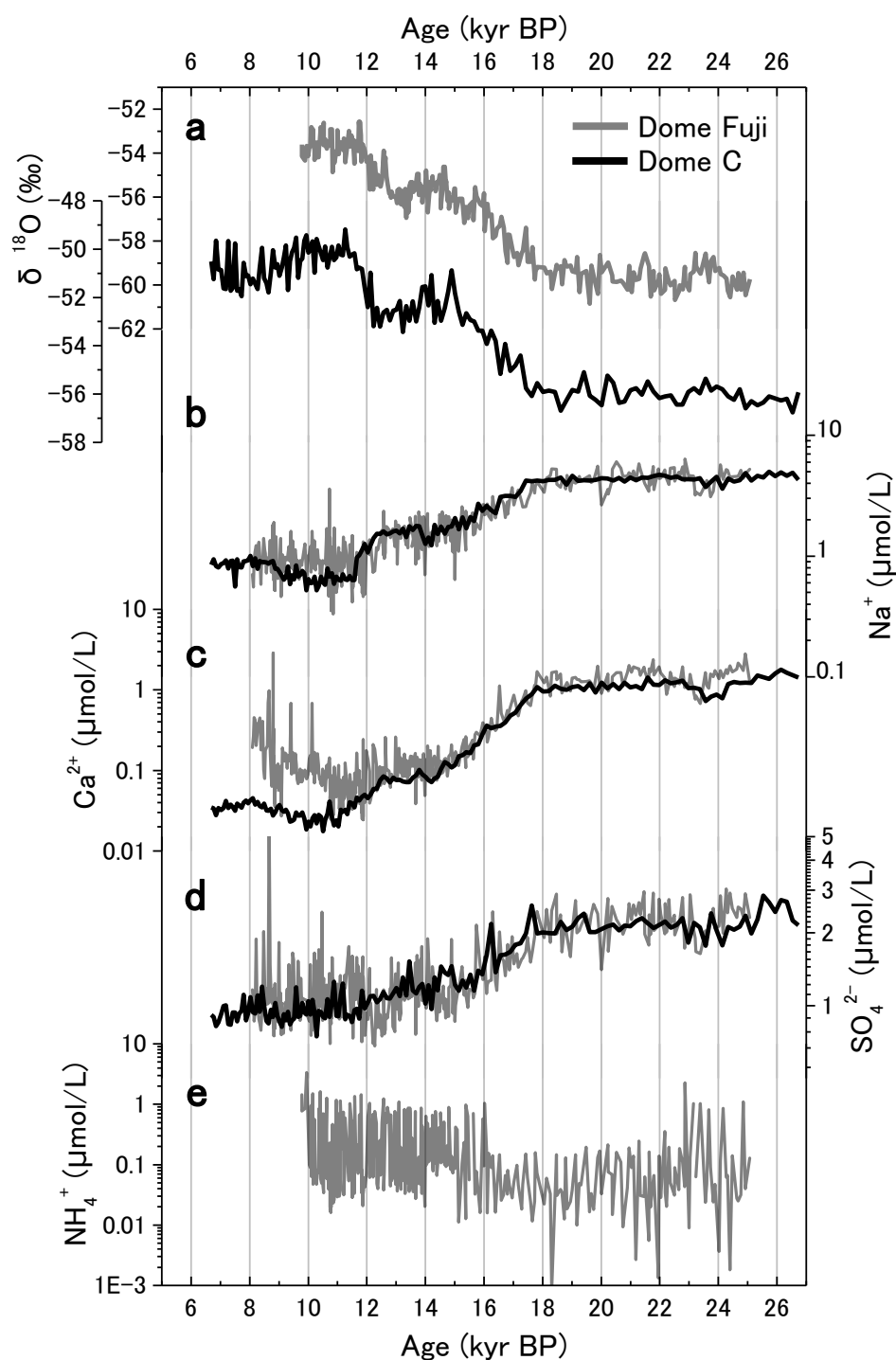


Figure 5.2.2 $\delta^{18}\text{O}$ and ion concentrations of the Dome Fuji and the Dome C ice cores. Gray indicates the Dome Fuji profiles, and black indicates the Dome C profiles. (a) $\delta^{18}\text{O}$. (b) Na^+ concentration. (c) Ca^{2+} concentration. (d) SO_4^{2-} concentration. (e) NH_4^+ concentration. NH_4^+ concentration is only the Dome Fuji.

5.2.3 Difference of Ca-salt fraction between Dome Fuji and Dome C

The major soluble salts in both Dome Fuji and Dome C ice cores are the same, and the ways of these changes are also similar to each other. However, the Ca-salt fraction in Dome Fuji is higher than that in Dome C. As described in sections 5.1.1 and 5.1.2, $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ ratio of the Dome Fuji ice core is below 1 for 25.0–16.8 kyr BP, whereas that of the Dome C ice core is above 1 in the same period. For 25–18 kyr BP, the Ca^{2+} concentration of Dome Fuji is higher than that of Dome C, whereas the Na^+ and SO_4^{2-} concentrations are almost same (Figure 5.2.2). Therefore, the lower $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ in Dome Fuji is probably because the Ca^{2+} concentration of Dome Fuji is higher than that of Dome C.

Fischer et al. [2007] showed that the non-sea-salt Ca^{2+} flux at EDML is about 3 times higher than at Dome C in the glacial period, and explained that the geographic location of EDML is much closer to South America and downwind of the cyclonically curved atmospheric pathway from Patagonia where the major source for Ca^{2+} in the glacial period is located [Reijmer et al., 2002]. Accordingly, they attribute the higher atmospheric nss Ca^{2+} concentrations at EDML to the greater proximity of EDML to the Patagonian dust source. The same idea may explain the different Ca^{2+} concentrations between Dome Fuji and Dome C. The geographic location of Dome Fuji from South America is farther than EDML, but much closer than Dome C, and some air parcels may come from the Patagonia region [Suzuki et al., 2008]. Difference of site location between Dome Fuji and Dome C is one of the possible reasons to explain the high Ca^{2+} concentration.

At the beginning of the Holocene (around 10 kyr BP), fractions of other-Ca and CaSO_4 of Dome Fuji remarkably increased (Figure 5.1.1a). After reaching a minimum Ca^{2+} concentration (0.03 $\mu\text{mol/L}$) at 11 kyr BP in Dome Fuji, the Ca^{2+} concentration increased (Figure 5.2.2c). This increase may have contributed to the increase of the other-Ca and CaSO_4 fractions around 10 kyr BP.

The Ca^{2+} increase around 10 kyr BP cannot be seen in the Dome C ice core (Figure 5.2.2c), so this behaviour might point to additional dust sources near to the Dome Fuji drill site becoming available at the beginning of the Holocene. In the early Holocene, the Ca^{2+} concentration in EDML also increased [Fischer et al., 2007]. A potential local source is the Sør-Rondane Mountains located at Dronning Maud Land. It is known that limestone and pure marble lenses are abundant especially in the western part of the range [e.g., Nakao et al., 2013]. Sakurai et al. [2011] also suggests that some of nss Ca^{2+} was transported from the Sør-Rondane Mountains. To clear the reason for the high Ca-salt fraction in the beginning of the Holocene, further study is needed.

5.3 Causes of the changes in the soluble salts in Greenland ice core

In this section, changes of the major soluble salts of NaCl, Na₂SO₄, CaSO₄ and CaCO₃ over the last termination in the NEEM ice core are discussed.

5.3.1 Last Glacial Maximum (LGM; 27.0–15.0 kyr BP)

In the coldest stage of the LGM, the Ca-salt fraction is 3.3 times higher than the Na-salt fraction. Since the Ca-salt and Na-salt are the major soluble non-volatile particles in the NEEM ice core, this feature indicates that most of the soluble non-volatile particles in the LGM consist of terrestrial material (Ca²⁺) in this stage. Also, the CaCO₃ fraction is high in the LGM. The major source of terrestrial material (Ca²⁺) in the LGM is Asian desert [De Angelis et al., 1997; Svensson et al., 2000; Fischer et al., 2007], so there may be sufficient time for Ca²⁺ to react with SO₄²⁻ due to long-range Ca²⁺ transportation; nevertheless a lot of CaCO₃ remained without sulfatization. This may be because the Ca²⁺ concentration was too high (5.56 µmol/L) compared to the SO₄²⁻ concentration (3.22 µmol/L) in the LGM (Figure 5.3.1, Table 5.4), so the SO₄²⁻ concentration was not enough to sulfatize all Ca²⁺. As a result, some part of CaCO₃ was not sulfatized and the CaCO₃ fraction was high in the LGM.

5.3.2 Bølling-Allerød (BA; 14.6–12.9 kyr BP)

During the interstadial stage of Bølling-Allerød (BA), the CaCO₃ fraction decreased, whereas the NaCl and Na₂SO₄ fractions increased from the LGM (Table 5.2; Figure 5.1.3). The contribution of Na-salt in the BA is higher than that in the LGM. This result may be due to a large reduction of Ca²⁺ concentration (Figure 5.3.2). The Ca²⁺ concentration decreased by a factor 6 from the LGM, whereas the Na⁺ concentration decreased by a factor 3.5 (the Ca²⁺ and Na⁺ concentrations in the LGM are 5.56 µmol/L and 3.36 µmol/L, respectively, and those in the BA are 0.95 µmol/L and 0.93 µmol/L, respectively) (Table 5.3). This difference caused the high Na-salt fraction in the BA. Moreover, the CaSO₄ and NaSO₄ fractions in the BA are higher than those in the LGM. This result indicates that sulfatization of Ca²⁺ and Na⁺ in the BA was more occurred than in the LGM.

5.3.3 Younger Dryas (YD; 12.6–12.0 kyr BP)

During the stadial stage of Younger Dryas (YD), the fractions of CaCO₃ and CaSO₄ increased,

whereas those of NaCl and Na₂SO₄ decreased from the BA. This may be because the Ca²⁺ concentration increased more than the Na⁺ concentration from the BA to the YD (Figure 5.3.2). The Ca²⁺ and Na⁺ concentrations of the YD are 3.12 μmol/L and 2.06 μmol/L, respectively (Table 5.4). The most distinct feature in the YD is a high CaSO₄ fraction (Figure 5.1.3a). The YD stage is a cold climate stage, and the situation is close to the LGM rather than the Holocene and BA. However, different from the LGM, the Ca²⁺ concentration is low compared to the SO₄²⁻ concentration (Figure 5.3.1, Table 5.4). The [Ca²⁺]/[SO₄²⁻] ratio of the YD is 1.16 and that of LGM is 1.79. Namely, the SO₄²⁻ concentration compared to the Ca²⁺ concentration is higher in the YD than that in the LGM. As a result, sulfatization of CaCO₃ may be more occurred in the YD than in the LGM, so that the CaSO₄ fraction was high in the YD.

5.3.4 Holocene (11.7 kyr BP ~)

In the warmest stage of the Holocene, the soluble salt composition is characterized by high Na-salt with high NaCl and Na₂SO₄ fractions. This feature indicates that soluble non-volatile particles consist of more sea-salt (Na⁺) than terrestrial material (Ca²⁺). The Ca²⁺ concentration decreased by a factor 30 from the LGM to the Holocene, whereas the Na⁺ concentration decreased by a factor 10 from the LGM to the Holocene, so that the mean Na⁺ concentration (0.47 μmol/L) is higher than the Ca²⁺ concentration (0.27 μmol/L) in the Holocene (Table 5.4). This difference caused the high Na-salt fraction. Also, the Holocene stage has a sufficient SO₄²⁻ concentration compared to the Ca²⁺ and Na⁺ concentrations ([SO₄²⁻] > [Ca²⁺] + [Na⁺]), so that the sulfatization of Na⁺ may have occurred most efficiently in 4 stages of the Holocene, YD, BA and LGM. As a result, the Na₂SO₄ fraction is the highest in 4 stages. However, despite [SO₄²⁻] > [Ca²⁺] + [Na⁺] like in inland Antarctica, more than half of Na-salt exists as NaCl. Namely, the Na⁺ sulfatization was increased, but differently from the Holocene in inland Antarctica, a lot of Na⁺ exists as primary salt (NaCl) in the Holocene Greenland. Possible reasons are as follows.

First, the NH₄⁺ in the Holocene in Greenland should be considered. The NH₄⁺ originated from NH₃ emissions, which have predominantly continental sources of biogenic origin [Fuhrer et al., 1993]. In Antarctica, the NH₄⁺ is a minor contribution because Antarctica is isolated from the continents which are the main source of NH₄⁺ [Legrand et al., 1997]. On the other hand, Greenland is surrounded by continents, so the mean level of NH₄⁺ is high [Legrand et al., 1997]. The NH₄⁺ concentration in Greenland started to increase from before the BA along with the retreating Laurentide ice sheet and spreading vegetation-covered area in North America, where the major source of NH₄⁺ for Greenland is

located [Fuhrer et al., 1996; Mayewski et al., 1997] (Figure 5.3.2, Table 5.3). Especially, the NH_4^+ concentration is higher than the Na^+ and Ca^{2+} concentrations in Holocene [Mayewski et al., 1997]. Namely, the NH_4^+ is the most dominant cation in the Holocene. The NH_4^+ has a peak in summer, which is consistent with a SO_4^{2-} peak. It has been known that the $(\text{NH}_4)_2\text{SO}_4$ arises from the neutralization of the SO_4^{2-} by NH_4^+ [Warneck, 1999; Fuhrer et al., 1996]. Thus, $(\text{NH}_4)_2\text{SO}_4$ formation may be dominant in summer season. In fact, Figure 4.2.2f in Chapter 4 suggests this increase of $(\text{NH}_4)_2\text{SO}_4$ in summer. Therefore, summer SO_4^{2-} and NH_4^+ may form $(\text{NH}_4)_2\text{SO}_4$, and the SO_4^{2-} concentration may be insufficient to form Na_2SO_4 in the subsequent winter (Na^+ peak). Figure 4.2.2e also supports this idea; the NaCl accounts for more than half of Na-salt in the winter season. In this way, the increase in NH_4^+ concentration in the Holocene and seasonal variations cause the high NaCl fraction in the Holocene in Greenland.

The differences of meteorological conditions and site locations between NEEM (Greenland) and Dome Fuji and Dome C (inland Antarctica) are also considered to be related to the high NaCl fraction in the Holocene in Greenland. The polar vortex over Antarctica is more pronounced and persistent than the Arctic one [Nash et al., 1996], and Dome Fuji and Dome C are situated at a distance of about 1000 km from the nearest coast at high altitude (more than 3200 m a.s.l), so the low pressures do not often travel to Dome Fuji and Dome C. On the other hand, the polar vortex over the Arctic often contains two low pressure centres, and the jet stream is meandering. Also, NEEM is situated at a distance of about 400 km from the nearest coast at 2450 m a.s.l (lower than Dome Fuji and Dome C), so the low pressures more often travel to the NEEM site compared to Dome Fuji and Dome C. Recent sea-salt depositions both in Greenland and Antarctica are closely connected to cyclone activity [Fischer et al., 2007], so the sea-salt can be more efficiently transported to Greenland. Due to the short transport distance of sea-salt and cyclone activity, the time to react sea-salt (NaCl) with H_2SO_4 may decrease. Moreover, due to the different seasonality between Na^+ and SO_4^{2-} , there may be not much H_2SO_4 in the atmosphere in winter when the sea-salt emission peaks (see Chapter 4). This behaviour may cause the high NaCl fraction in the NEEM ice core. In the Antarctic ice core study, Talos Dome, a peripheral dome, contains more NaCl than Dome Fuji in the warm period [Iizuka et al., 2013]. One of the potential reasons is the short transport distance of marine-sourced aerosol, which reduced the time of reaction for NaCl and H_2SO_4 before reaching Talos Dome. The locational condition of NEEM may be one of the causes of the high NaCl fraction.

Finally, the higher accumulation rate in Greenland is also one of the potential reasons for the high NaCl fraction in the NEEM ice core. In inland Antarctica, post-depositional reaction of NaCl with

H_2SO_4 is enhanced due to low accumulation rates [Röthlisberger et al., 2003b]. However, higher accumulation rates prevent post-depositional reaction because they lead to less sublimation of snow and acid at the snow surface [Kameda et al., 2008]. Less snow sublimation means that less H_2SO_4 and NaCl migrate from the inside to the surface of the snow crystals, thus providing less chance of contact between the acid and salt [Iizuka et al., 2013]. The accumulation rate of the present NEEM site is about 10 times higher than that in inland Antarctica. Thus, the higher accumulation rate at NEEM is also one of the potential reasons for the high NaCl fraction in the NEEM ice core in the Holocene.

Table 5.4 Ion concentrations in Greenland ice cores ($\mu\text{eq/L}$).

Ca^{2+} , Na^+ , and SO_4^{2-} are concentrations in the NEEM ice core [Fischer et al; Mulvaney et al., personal communications]. NH_4^+ concentration is from the GISP2 ice core [Mayewski et al., 1997].

		Ca^{2+}	Na^+	SO_4^{2-}	NH_4^+
Holocene	mean	0.53	0.47	1.81	0.65
	std. dev.	0.18	0.07	0.61	0.44
YD	mean	6.24	2.06	5.37	0.90
	std. dev.	1.73	0.29	2.25	0.48
BA	mean	1.89	0.93	2.59	0.69
	std. dev.	0.65	0.28	0.90	0.55
LGM	mean	11.11	3.36	6.43	0.28
	std. dev.	2.43	0.07	1.03	0.09

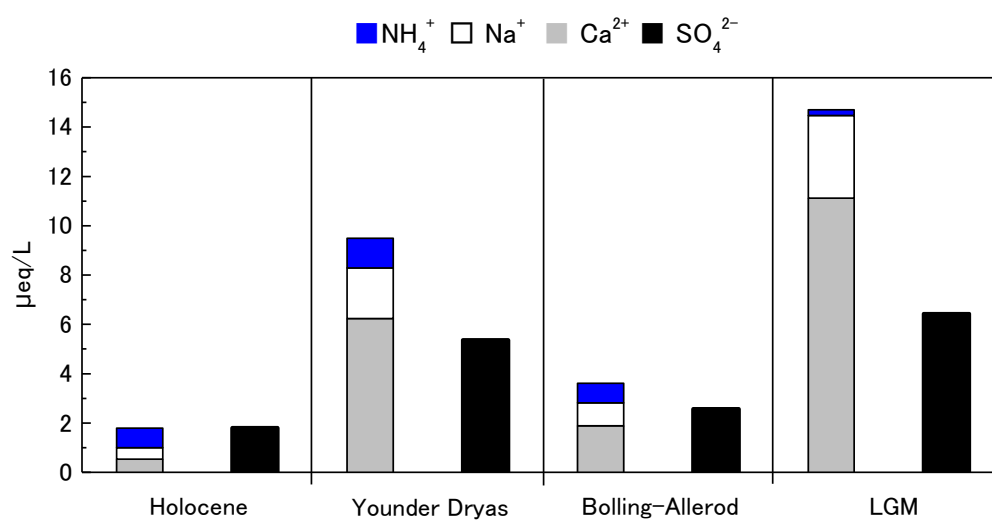


Figure 5.3.1 Ionic balance of Na^+ , Ca^{2+} and SO_4^{2-} in the Holocene, YD, BA, and LGM in the NEEM ice core.

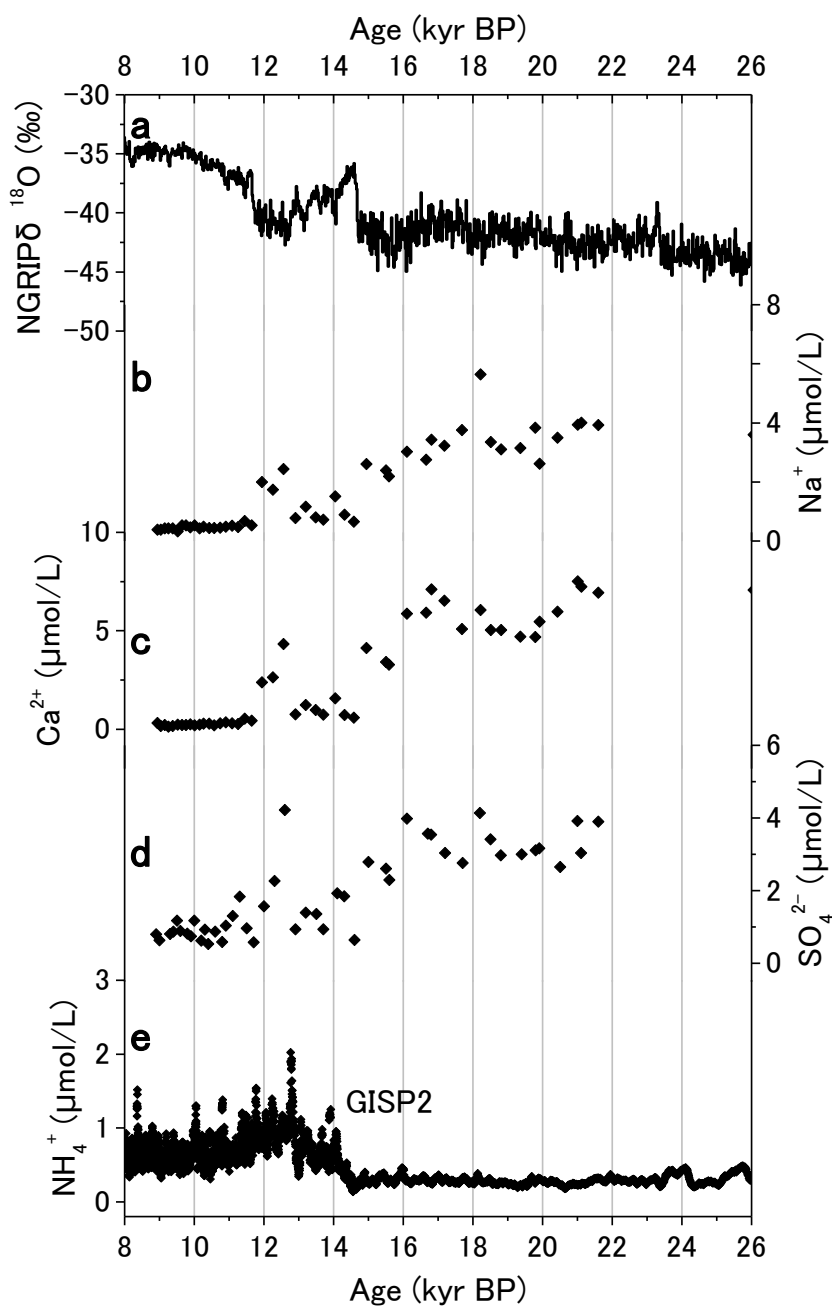


Figure 5.3.2 Water isotope and ion concentrations of the Greenland ice cores. (a) $\delta^{18}\text{O}$ of the NGRIP ice core [Rasmussen et al., 2014]. (b) Na^+ concentration of the NEEM ice core [Fischer et al., personal communication]. (c) Ca^{2+} concentration of the NEEM ice cores [Fischer et al., personal communication]. (d) SO_4^{2-} concentration of the NEEM ice cores [Mulvaney et al., personal communication]. (e) NH_4^+ concentration in GISP2 [Mayewski et al., 1997].

CHAPTER 6

6 Bipolar sulfate-salt fluxes and temperature changes during the last termination

Since the sublimation method provides only fractions of non-volatile particles, salt concentrations must be calculated under several assumptions. In the first half of this chapter, previous ion-deduced methods are examined by sublimation results, then the best ion-deduced method for Antarctica is proposed. For Greenland, another calculation method is proposed because the ion-deduced method for Antarctica cannot be applied. Using these calculation methods, salt concentrations, especially sulfate salt concentrations are derived. The latter part of this chapter discusses relationships between sulfate-salt fluxes and temperature changes during the last termination.

6.1 Salts calculation method for the Antarctic ice cores

In this section, previous ion-deduced method of Case I to III are examined by using the sublimation results of the Dome Fuji and Dome C ice core described in Chapter 5, then the new ion-deduced method as Case IV is suggested. The Case I to III are formulated based on the previous studies. Case I is assuming that the Na^+ forms NaCl prior to Na_2SO_4 . This case produces NaCl when the Cl^-/Na^+ ratio is close to the sea-water ratio (1.8 [Whitlow et al., 1992]) as Legrand et al. [1988] and Röthlisberger et al. [2003b] suggested. Case II is assuming that the Ca^{2+} forms sulfate prior to nitrate and before the Na^+ forms sulfate, whereas Na^+ forms Na_2SO_4 prior to NaCl. This case is based on ideas from previous studies such as Röthlisberger et al. [2003b], Iizuka et al. [2008], and Sakurai et al. [2011]. Case III is assuming that the Ca^{2+} forms nitrate prior to sulfate. This case is based on an implication of Röthlisberger et al. [2000]. Detailed calculation formulae were described in Chapter 2.

6.1.1 Validity of the previous ion-deduced methods

Comparisons between the sublimation-EDS method and Case I of the ion-deduced method are

plotted in Figure 6.1.1a and 6.1.1b for the Dome Fuji ice core, and Figure 6.1.2a and 6.1.2b for the Dome C ice core. For the $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ ratio, Figure 6.1.1a shows the slope as 0.35 with a low correlation ($R^2 = 0.19$), and Figure 6.1.1b shows the $\text{NaCl}/\text{Na}_2\text{SO}_4$ 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 in the Dome Fuji ice core. Similar results are obtained also from the Dome C ice core. The results of the micro-Raman method of the Dome Fuji ice core [Sakurai et al., 2011] and the sublimation-EDS method of the Dome Fuji and Dome C ice cores showed that Na_2SO_4 exists not only in the latter half of the last termination (16–11 kyr BP), but before as well (see Chapters 3 and 5); however, the estimated values from Case I do not show the Na_2SO_4 in the first half of the last termination (25–16 kyr BP).

The value of Cl^-/Na^+ of 25–16 kyr BP is close to the sea-water ratio both in the Dome Fuji and Dome C ice cores (Figure 6.1.3). This implies under the Case I 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 Na_2SO_4 exists even when the Cl^-/Na^+ close to the sea-water ratio. Thus the assumption about Na^+ of Case I, in which Na^+ forms NaCl when the Cl^-/Na^+ ratio is near the sea-water ratio, is not appropriate. The Cl^-/Na^+ ratio is close to the sea-water ratio during 25–16 kyr BP, yet some Na^+ must form Na_2SO_4 instead of NaCl. The presence of Na_2SO_4 indicates that not all Cl^- forms NaCl. In other words, some of Cl^- should be in the form of HCl and/or other chloride salts during this period. The HCl cannot be detected because HCl volatilizes during the sublimation, but Cl-containing particles were found (e.g., with MgCl_2). The results, therefore, suggest that a certain amount of NaCl reacted to Na_2SO_4 even if the Cl^-/Na^+ ratio close to sea water ratio.

In contrast, Case II correlates well with the sublimation-EDS method. For the molar ratios of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ of the Dome Fuji ice core, the slope is 0.96 with a high correlation ($R^2 = 0.86$) (Figure 6.1.1c). For the same ratios of the Dome C ice core, the slope is 0.71 with a high correlation ($R^2 = 0.81$) (Figure 6.1.2c). These nearly 1:1 relationships suggest that Case II deduces CaSO_4 and Na_2SO_4 concentrations accurately. For $\text{NaCl}/\text{Na}_2\text{SO}_4$, the slope is 0.89 with a high correlation $R^2 = 0.50$ in Dome Fuji (Figure 6.1.1d), and the slope is 1.12 with a high correlation $R^2 = 0.61$ in Dome C (Figure 6.1.2d). However, Case II underestimates the NaCl concentration for 16–11 kyr BP, giving a value of zero both in the Dome Fuji and Dome C ice cores, because $[\text{SO}_4^{2-}]$ exceeds the sum of $[\text{Ca}^{2+}]$ and $[\text{Na}^+]$. Thus, Case II poorly reconstructs NaCl concentration during the warm period.

For the Case III, the slope of the molar ratios of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ of the Dome Fuji ice core is 0.21 with correlation ($R^2 = 0.54$) (Figure 6.1.1e), and that of the Dome C ice core is 0.75 with high correlation ($R^2 = 0.62$) (Figure 6.1.2e). The slope of the molar ratios of $\text{NaCl}/\text{Na}_2\text{SO}_4$ of the Dome

Fuji ice core is 44.0 with no correlation ($R^2 = 0.06$) (Figure 6.1.1e), and that of the Dome C ice core is 1.30 with correlation ($R^2 = 0.43$) (Figure 6.1.2e). It should be note that 13 data points of the Dome Fuji ice core and 4 data point of the Dome C ice core are not plotted on the Figure 6.1.1e and 6.1.2e, because CaSO_4 concentration derived as 0. However, the sublimation-EDS and the micro-Raman methods found CaSO_4 at all depth during the last termination (Chapters 3 and 5) (Figure 3.4.1, 5.1.1 and 5.1.2). Therefore, the Case III predicts CaSO_4 concentration that is too low. This makes the Na_2SO_4 concentration of Case III too high and the NaCl concentrations of Case III too low. As a result, the molar ratio of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ of Case III is too high and that of $\text{NaCl}/\text{Na}_2\text{SO}_4$ of Case III is too low both in the Dome Fuji and Dome C ice cores. Thus, Case III is not supported by the salt-compositions data from the sublimation-EDS method which discussed in Chapters 3 and 5.

6.1.2 New ion-deduced method including seasonal variation

I now propose a new deducing method based from Case II, to be called Case IV. The reason why the $\text{NaCl}/\text{Na}_2\text{SO}_4$ of Case II was lower than that of sublimation result in warm period may be related to the seasonality of atmospheric aerosol as discussed in Chapter 4. According to the monthly ionic balance of present aerosol, certain amount of Na^+ probably exists as NaCl . In this study, using 0.23 as a factor for the abundance ratio of NaCl , calculation method is formulated.

Case IV: This follows Case II, except I assume that 23% per year of Na^+ exists as NaCl for 16.3–11.0 kyr BP. If $[\text{Ca}^{2+}] > [\text{SO}_4^{2-}]$, then

$$[\text{CaSO}_4] = [\text{SO}_4^{2-}],$$

$$[\text{Na}_2\text{SO}_4] = 0,$$

$$[\text{NaCl}] = [\text{Na}^+] + [\text{Ca}^{2+}] - [\text{SO}_4^{2-}] - [\text{NO}_3^-].$$

When this gives $[\text{NaCl}] > [\text{Cl}^-]$, I assume $[\text{NaCl}] = [\text{Cl}^-]$, and

when this instead gives $[\text{NaCl}] \leq 0$, then $[\text{NaCl}] = 0$.

If $[\text{Ca}^{2+}] < [\text{SO}_4^{2-}]$ and $[\text{Ca}^{2+}] + [\text{Na}^+] > [\text{SO}_4^{2-}]$, I assume

$$[\text{CaSO}_4] = [\text{Ca}^{2+}],$$

$$[\text{Na}_2\text{SO}_4] = [\text{SO}_4^{2-}] - [\text{Ca}^{2+}], \text{ and}$$

$$[\text{NaCl}] = [\text{Na}^+] + [\text{Ca}^{2+}] - [\text{SO}_4^{2-}] - [\text{NO}_3^-].$$

When this gives $[\text{NaCl}] > [\text{Cl}^-]$, I assume $[\text{NaCl}] = [\text{Cl}^-]$, and

when this gives $[\text{NaCl}] \leq 0$, I set $[\text{NaCl}] = 0$.

If $[\text{Ca}^{2+}] + [\text{Na}^+] < [\text{SO}_4^{2-}]$ (16.3–11.0 kyr BP), then

$$\begin{aligned}[\text{CaSO}_4] &= [\text{Ca}^{2+}], \\ [\text{Na}_2\text{SO}_4] &= [\text{Na}^+] - 0.23[\text{Na}^+], \text{ and} \\ [\text{NaCl}] &= 0.23[\text{Na}^+].\end{aligned}$$

For the Dome Fuji ice core, the resulting $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratios from Case IV fit the sublimation-EDS method (Figure 6.1.1h) better than those from Case II. Both the slope and the R^2 value have improved. Also, most of plots are on the 1:1 line within the margin of errors. For the $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ ratio, the ratio from Case IV also agrees well with the sublimation-EDS method, with a regression slope of 0.84 ± 0.07 and $R^2 = 0.82$ (Figure 6.1.1g). Thus, the Case IV method reproduces not only CaSO_4 and Na_2SO_4 concentrations 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 kyrs.

Case IV was also applied to calculate salts concentrations of the Dome C ice core. The slope of the molar ratio of $\text{Na}_2\text{SO}_4/\text{CaSO}_4$ is 0.63 with high correlation ($R^2 = 0.80$), and that of $\text{NaCl}/\text{Na}_2\text{SO}_4$ is 1.15 with high correlation ($R^2 = 0.60$) (Figure 6.1.2). For the CaSO_4 and Na_2SO_4 , most of plots are on the 1:1 line within the margin of error, on the other hand, several plots of $\text{NaCl}/\text{Na}_2\text{SO}_4$ are not on the 1:1 line. The calculation of CaSO_4 and Na_2SO_4 does not need many assumptions, so the CaSO_4 and Na_2SO_4 concentrations can be reliable. However, the deducing of NaCl concentration needs further factors. Thus, the NaCl concentration in the Dome C ice core may have high uncertainty, which indicates that the deducing of NaCl concentration is difficult by using only ion concentrations (the sublimation study is needed).

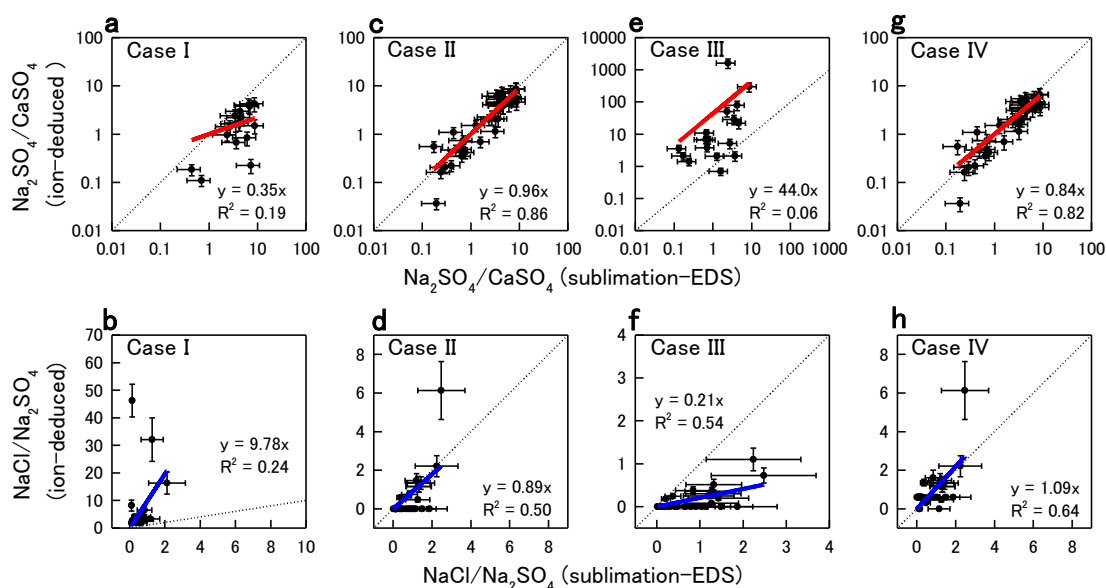


Figure 6.1.1 Comparison of four ion-deduced methods to the sublimation-EDS method on the Dome Fuji ice core. Top row is the molar ratio $\text{Na}_2\text{SO}_4/\text{CaSO}_4$, bottom row is $\text{NaCl}/\text{Na}_2\text{SO}_4$. (a) and (b): Case I ion-deduced method. (c) and (d) Case II. (e) and (f) Case III. (g) and (h) Case IV. The solid lines are the linear fitting lines. Dotted lines mark the 1:1 relation. Note that 13 data points are not plotted in (e) because $\text{CaSO}_4 = 0$. (Number of datapoints $n = 35$ for a, b, c and g, and $n = 30$ for d, e, f, and h. Of the 39 particle samples, 4 had no corresponding ion measurement at the same depth and 5 had an anomalous value of NO_3^-).

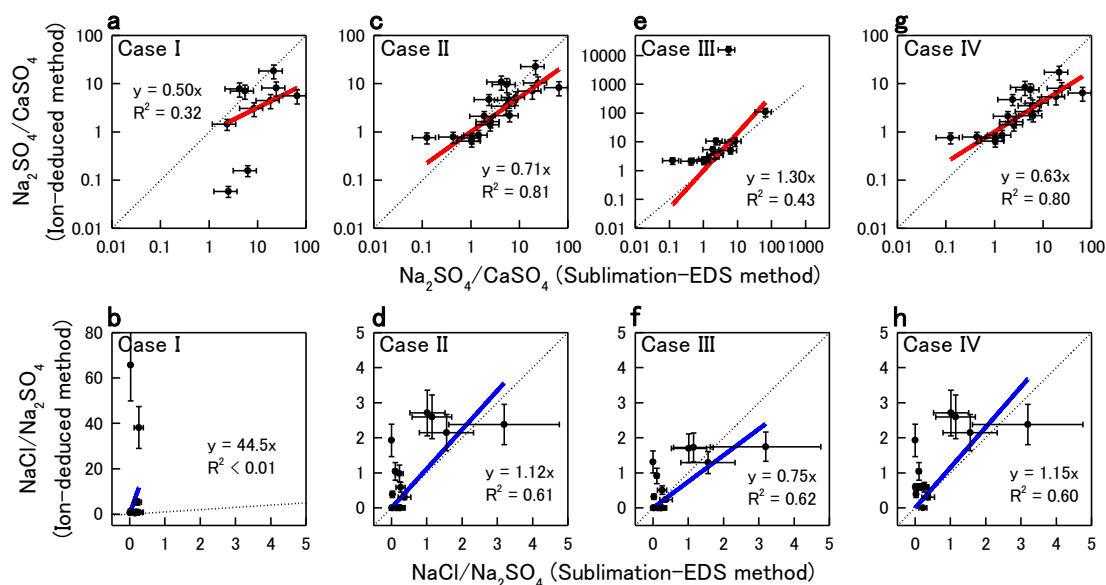


Figure 6.1.2 This figure is the same as Figure 6.1.1 except that is shown the Dome C ice core. Number of data points $n = 19$. Note that 4 data points are not plotted in (e) because $\text{CaSO}_4 = 0$.

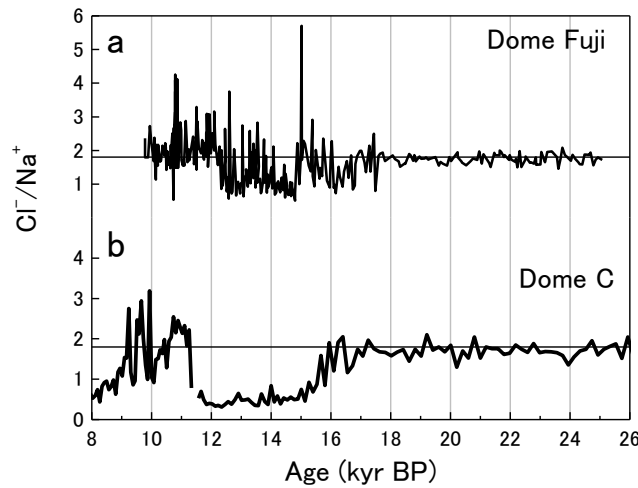


Figure 6.1.3 Concentration ratios of Cl^- to Na^+ (ppb/ppb). (a) Ratio of the Dome Fuji ice core. (b) Ratio of the Dome C ice core. Vertical lines in a and b are sea-water ratio 1.8 [Whitlow et al., 1992]

6.2 Salts calculation method for the NEEM ice core

The ion-deduced method for inland Antarctica cannot be applied to Greenland. The reasons are that 1) in inland Antarctica, sulfatization of Ca^{2+} and Na^+ occurs almost in equilibrium state (mainly consist of secondary aerosols); 2) in Greenland, sulfatization of Ca^{2+} and Na^+ may not fully occur as discussed in Chapter 5 (mainly consist of primary aerosols). Also, NH_4^+ should be considered in the Holocene as a summer composition as indicated in Chapter 4. The three components (NaCl , Na_2SO_4 and CaSO_4) are the major soluble salts in Antarctica, whereas four components (NaCl , Na_2SO_4 , CaSO_4 and CaCO_3) are the major components in Greenland as shown in Chapters 3 and 5. Thus, more things should be taken into account to calculate salt concentration for Greenland ice cores compared to inland Antarctica. Here, salt concentrations of the NEEM ice core are calculated by using molar mass ratios that result from the sublimation method. The CaSO_4 , CaCl_2 , other-Ca, Na_2SO_4 , NaCl , and other-Na can be considered as soluble, thus $[\text{Ca}^{2+}]$ is equivalent to $[\text{CaSO}_4] + [\text{CaCl}_2] + [\text{other-Ca}]$, and $[\text{Na}^+]$ is equivalent to $[\text{Na}_2\text{SO}_4] + [\text{NaCl}] + [\text{other-Na}]$. “other-S” indicates sulfate salts other than CaSO_4 , Na_2SO_4 , MgSO_4 and K_2SO_4 . Star symbols (*) indicate masses obtained by EDS results as described in section 2.2.3. The calculation formulae are as follows:

$$[\text{CaSO}_4] = [\text{Ca}^{2+}] \times \frac{[*\text{CaSO}_4]}{[*\text{CaSO}_4] + [*\text{CaCl}_2] + [*\text{other-Ca}]},$$

$$[\text{Na}_2\text{SO}_4] = [\text{Na}^+] \times \frac{[*\text{Na}_2\text{SO}_4]}{[*\text{Na}_2\text{SO}_4] + [* \text{NaCl}] + [* \text{other-Na}]},$$

$$[\text{Sulfate-salt}] = ([\text{CaSO}_4] + [\text{Na}_2\text{SO}_4]) \times \frac{[* \text{Total sulfate-salt}]}{[* \text{CaSO}_4] + [* \text{Na}_2\text{SO}_4]},$$

$$[* \text{Total sulfate-salt}] = [* \text{CaSO}_4] + [* \text{Na}_2\text{SO}_4] + [* \text{MgSO}_4] + [* \text{K}_2\text{SO}_4] + [* \text{other-S}]$$

$$[\text{CaCO}_3] = [\text{Ca}^{2+}] \times \frac{[* \text{exCa}]}{[* \text{CaSO}_4] + [* \text{CaCl}_2] + [* \text{other-Ca}]},$$

$$[\text{NaCl}] = [\text{Na}^+] \times \frac{[* \text{NaCl}]}{[* \text{Na}_2\text{SO}_4] + [* \text{NaCl}] + [* \text{other-Na}]}$$

6.3 Salt fluxes during the last termination in Antarctica and Greenland

This section describes salt fluxes of the Dome Fuji, Dome C and NEEM ice cores derived by calculation methods as described in section 6.1 and 6.2.

6.3.1 Salt fluxes of the Dome Fuji ice core

The temperature change in the Antarctica during the last termination is consist of 5 phases; Phase I (25.0–18.0 kyr BP; LGM to pre-initiation of warming), Phase II (18.0–14.7 kyr BP; First warming step), Phase III (14.7–12.7 kyr BP; Antarctic Cold Reversal (ACR)), Phase IV (12.7–11.7 kyr BP; Second warming step), and Phase V (11.7 kyr BP~; Holocene). The CaSO_4 , Na_2SO_4 , and NaCl fluxes of Dome Fuji ice core calculated by Case IV are shown in Figure 6.3.1. The CaSO_4 flux shows the high value of $3.1 \pm 0.8 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Phase I, then decreases dramatically in Phase II. In Phase III to V, the flux stays low at $0.3 \pm 0.2 \text{ mg m}^{-2} \text{ yr}^{-1}$. In contrast, low value of Na_2SO_4 flux ($1.8 \pm 0.7 \text{ mg m}^{-2} \text{ yr}^{-1}$) in Phase I slightly increases in Phase II, reaching a high value of $2.8 \pm 0.4 \text{ mg m}^{-2} \text{ yr}^{-1}$ around 16.0 kyr BP. After 16.0 kyr BP, this flux decreased. In the Phase III, the decreasing stopped and the flux stayed at $2.2 \pm 0.6 \text{ mg m}^{-2} \text{ yr}^{-1}$. In Phase IV, the Na_2SO_4 flux decreased again, and reached the low value of $1.6 \pm 0.4 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Phase V. The NaCl flux has a relatively high value ($0.7 \pm 0.5 \text{ mg m}^{-2} \text{ yr}^{-1}$) in Phase I. Then this flux becomes low ($0.4 \pm 0.2 \text{ mg m}^{-2} \text{ yr}^{-1}$) in Phase II to V. The total sulfate-salt flux (CaSO_4 plus Na_2SO_4) having a high value of $4.9 \pm 0.8 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Phase I decreased in Phase II. In the Phase III, the decreasing stopped and the sulfate-salt flux stayed at $2.6 \pm 0.6 \text{ mg m}^{-2} \text{ yr}^{-1}$. In the Phase IV, the flux decreased again, and reached the low value of $1.8 \pm 0.5 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Phase V.

6.3.2 Salt fluxes of the Dome C ice core

The CaSO_4 , Na_2SO_4 , NaCl , and sulfate-salt fluxes of Dome C ice core calculated by Case IV are shown in Figure 6.3.1. Changes in the CaSO_4 , Na_2SO_4 , NaCl and sulfate-salt fluxes of Dome C ice are similar to those of Dome Fuji result. The CaSO_4 flux shows the high value of $2.0 \pm 0.3 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Phase I, then decreases dramatically in Phase II. In Phase III to V, the flux stays low at $0.2 \pm 0.1 \text{ mg m}^{-2} \text{ yr}^{-1}$. In contrast, low value of Na_2SO_4 flux ($1.6 \pm 0.3 \text{ mg m}^{-2} \text{ yr}^{-1}$) in Phase I increased in Phase II, reaching a high value of $2.7 \pm 0.3 \text{ mg m}^{-2} \text{ yr}^{-1}$ around 16.0 kyr BP. After 16.0 kyr BP, this flux decreased. In the Phase III, the decreasing stopped and the flux stayed at $1.8 \pm 0.1 \text{ mg m}^{-2} \text{ yr}^{-1}$. In Phase IV, the Na_2SO_4 flux decreased again, and reached the low value of $1.0 \pm 0.1 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Phase V. The NaCl flux has a relatively high value ($1.1 \pm 0.3 \text{ mg m}^{-2} \text{ yr}^{-1}$) in Phase I. Then this flux decreased between 18.0 and 16.0 kyr BP in Phase II. In the Phase III to V, the NaCl flux stayed at low value ($0.4 \pm 0.1 \text{ mg m}^{-2} \text{ yr}^{-1}$). The total sulfate-salt flux (CaSO_4 plus Na_2SO_4) having a high value of $4.1 \pm 0.4 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Phase I decreased in Phase II. In the Phase III, the decreasing stopped and the sulfate-salt flux stayed at $2.0 \pm 0.1 \text{ mg m}^{-2} \text{ yr}^{-1}$. In the Phase IV, the flux decreased again, and reached the low value of $1.1 \pm 0.1 \text{ mg m}^{-2} \text{ yr}^{-1}$ in Phase V.

Ways of changes in CaSO_4 , Na_2SO_4 , NaCl and sulfate-salt flux during the last termination in Dome C are similar to those of Dome Fuji. Timings of changes in these salts are well consistent with those of Dome Fuji within the margin of error of the time scale. Probably, changes in the CaSO_4 , Na_2SO_4 , NaCl and sulfate-salt flux are almost uniform in inland Antarctica during the last termination. However, as discussed in Chapter 5, CaSO_4 concentration of LGM in Dome Fuji ice is higher than that of Dome C ice.

6.3.3 Salt fluxes of the NEEM ice core

The CaCO_3 , CaSO_4 , NaCl , Na_2SO_4 , sulfate-salt fluxes of NEEM ice core are shown in Figure 6.3.2. Except Na_2SO_4 flux, salts fluxes show similar fluctuations. High flux in LGM decreased in Bølling-Allerød (BA), the flux slightly increased in Younger Dryas (YD), and then decreased to low in Holocene. Average flux of CaCO_3 at each stage is 15.2 ± 4.7 , 3.5 ± 0.7 , 8.1 ± 6.4 , and $2.3 \pm 0.8 \text{ mg m}^{-2} \text{ yr}^{-1}$ in LGM, BA, YD, and Holocene, respectively. The CaSO_4 flux is 7.6 ± 2.9 , 3.4 ± 2.6 , 9.9 ± 3.4 , and $1.4 \pm 1.1 \text{ mg m}^{-2} \text{ yr}^{-1}$ in LGM, BA, YD, and Holocene, respectively. The NaCl flux is 5.7 ± 1.3 , 2.3 ± 0.9 , 4.9 ± 1.9 , and $2.0 \pm 0.8 \text{ mg m}^{-2} \text{ yr}^{-1}$ in LGM, BA, YD, and Holocene, respectively. Differences of the Na_2SO_4 flux between each climatic stage are smaller than those of the other salts.

The Na_2SO_4 flux having relatively high in LGM decreased gradually toward Holocene. The Na_2SO_4 flux is 3.7 ± 2.0 , 3.0 ± 2.5 , 2.9 ± 2.1 , and $2.8 \pm 1.7 \text{ mg m}^{-2} \text{ yr}^{-1}$ in LGM, BA, YD, and Holocene, respectively. Change in the total sulfate-salt flux is similar to that of CaCO_3 , CaSO_4 , and NaCl fluxes. High flux in LGM decreased in BA, the flux slightly increased in YD, and then decreased to low in Holocene. The sulfate-salt flux is 17.6 ± 5.3 , 11.4 ± 5.7 , 14.9 ± 5.8 , and $6.8 \pm 3.2 \text{ mg m}^{-2} \text{ yr}^{-1}$ in LGM, BA, YD, and Holocene, respectively.

6.3.4 Difference of the ratios between the LGM and the Holocene in the NEEM and inland Antarctic ice cores

Absolute salt fluxes of the NEEM, Dome Fuji and Dome C ice cores were compared. The CaCO_3 , CaSO_4 , NaCl and Na_2SO_4 fluxes in the NEEM ice core are higher than those in the Dome Fuji and Dome C ice cores (Figure 6.3.3). Table 6.3 shows the ratios of each salt between the LGM and the Holocene in the Dome Fuji, Dome C and NEEM ice cores. The ratios of the Na-salts (NaCl and Na_2SO_4) are the almost same as in the three ice cores. On the other hand, the ratio of Ca-salts (CaCO_3 and CaSO_4) in the NEEM ice core is about two times larger than that in the Dome Fuji and Dome C ice cores. The fluxes of CaCO_3 , CaSO_4 and NaCl of the three ice cores in the LGM are significantly higher than in the Holocene, whereas Na_2SO_4 fluxes of the three ice cores are not changed from the LGM to the Holocene.

Table 6.3 Ratios of salt fluxes in the Dome Fuji, Dome C and NEEM ice cores between the LGM and the Holocene.

LGM/Holocene	CaCO_3	CaSO_4	NaCl	Na_2SO_4	Sulfate-salt
DF	—	10.3 ± 4.0	1.8 ± 2.5	1.1 ± 1.8	2.9 ± 1.2
DC	—	10.0 ± 3.0	2.8 ± 2.0	1.6 ± 3.0	3.4 ± 1.4
NEEM	6.6 ± 5.9	5.4 ± 2.6	2.9 ± 1.6	1.3 ± 1.2	2.6 ± 1.9

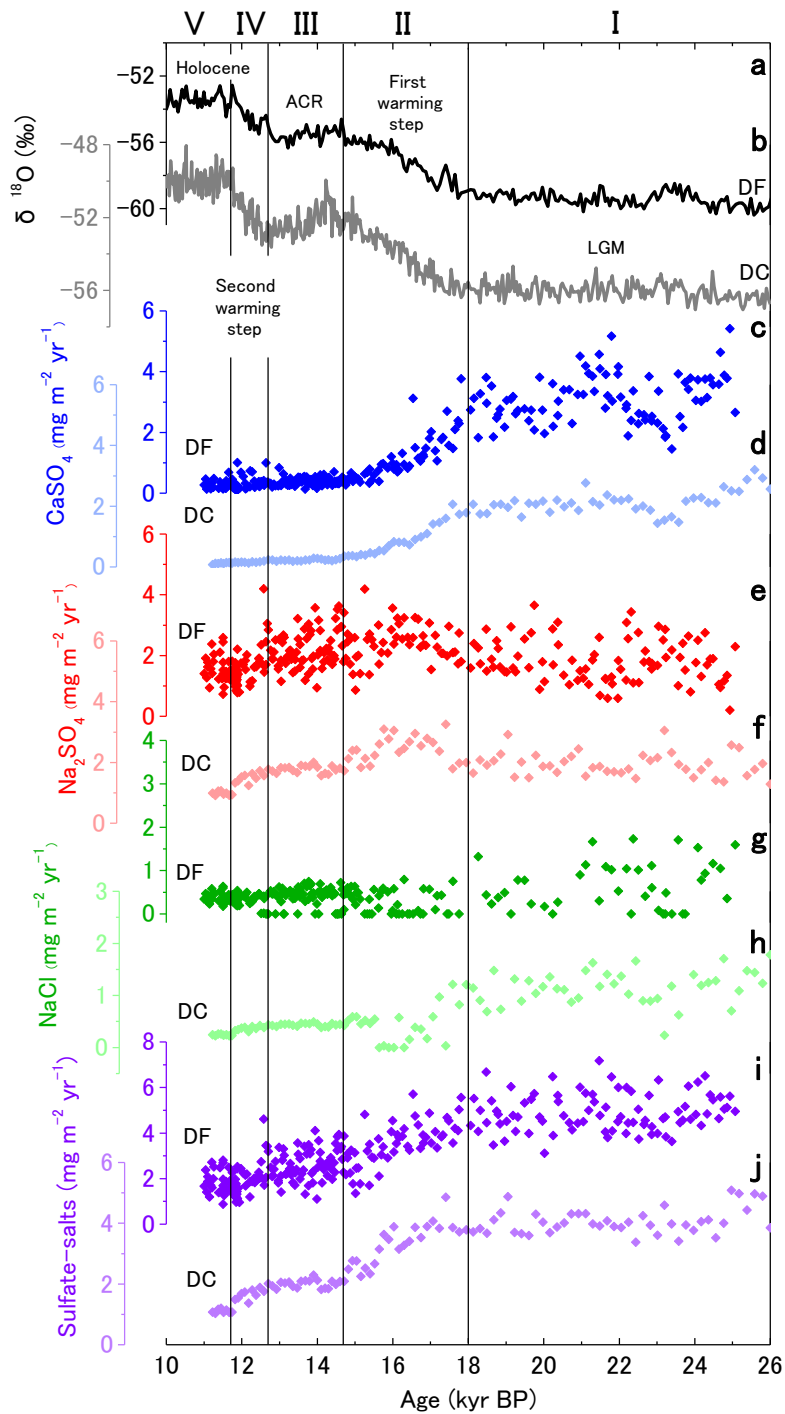


Figure 6.3.1 Time series salt fluxes of the Dome Fuji and the Dome C ice cores derived using the Case IV ion-deduced method. Darker colors indicate the Dome Fuji profile and lighter colors indicate the Dome C profile. (a) $\delta^{18}\text{O}$ of Dome Fuji [Watanabe et al., 2003a] (b) $\delta^{18}\text{O}$ of Dome C [Stenni et al., 2006]. Time scale is determined by EDC3 age model. (c) and (d) CaSO_4 flux of Dome Fuji and Dome C. (e) and (f) Na_2SO_4 flux of Dome Fuji and Dome C. (g) and (h) NaCl flux of Dome Fuji and Dome C. (i) and (j) Total sulfate-salt ($\text{CaSO}_4 + \text{Na}_2\text{SO}_4$) flux of Dome Fuji and Dome C. Vertical lines mark 18.0, 14.7, 12.7 and 11.7 kyr BP.

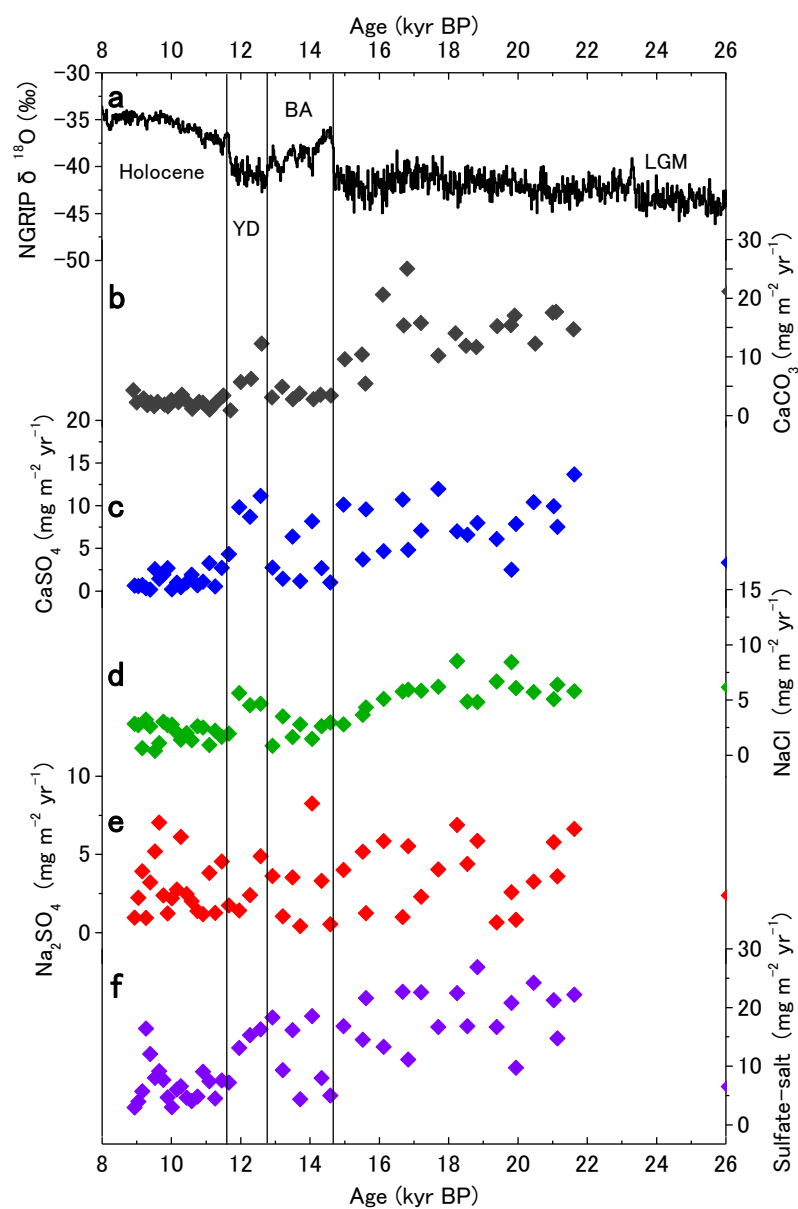


Figure 6.3.2 Time series salt fluxes of the NEEM ice core. (a) $\delta^{18}\text{O}$ profile of the NGRIP ice core [Rasmussen et al., 2014]. (b) CaCO_3 flux. (c) CaSO_4 flux. (d) NaCl flux. (e) Na_2SO_4 flux. (f) Total sulfate-salt flux. Vertical lines mark LGM, YD, BA and Holocene.

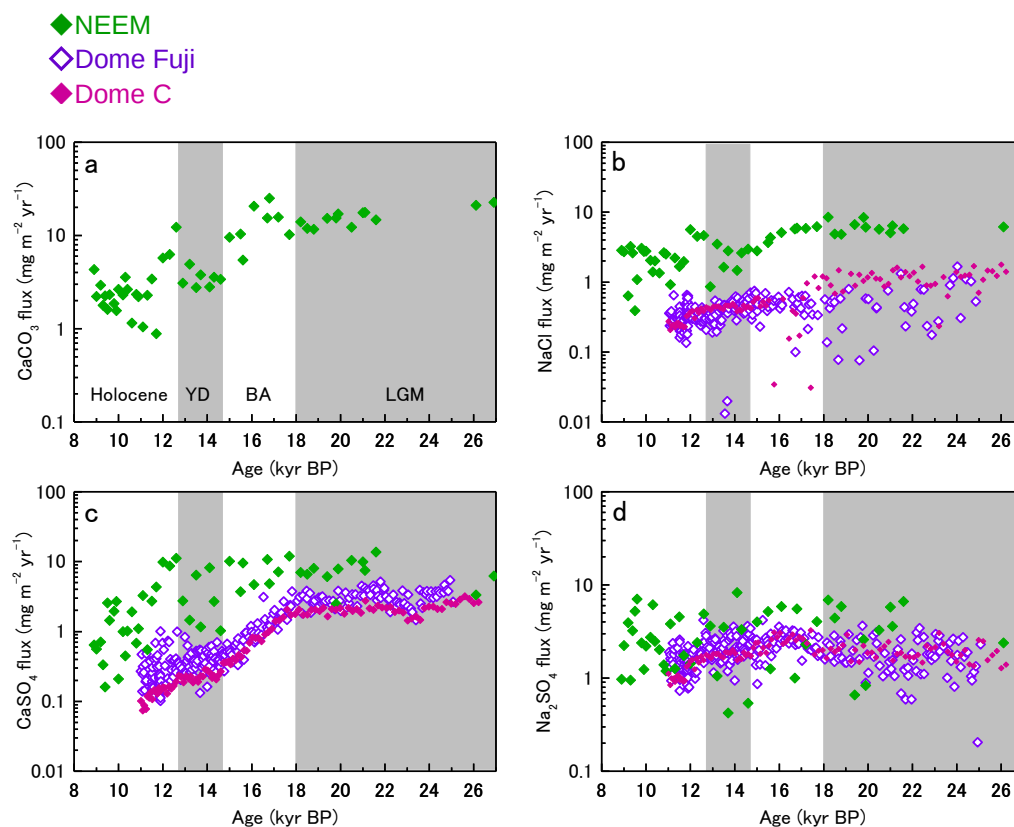


Figure 6.3.3 Time series of salt fluxes of the NEEM, Dome Fuji and Dome C ice cores. (a) CaCO_3 flux. (b) NaCl flux. (c) CaSO_4 flux. (d) Na_2SO_4 flux.

6.3.5 H₂SO₄ flux of the Dome Fuji, Dome C and NEEM ice cores

Previous studies found by using micro-Raman spectroscopy that sulfuric acid (H₂SO₄) is preserved in Antarctic ice [Fukazawa et al., 1998; Ohno et al., 2005]. From this study, some of SO₄²⁻ can be assumed to be present as H₂SO₄ especially in warm periods. Figure 6.3.4 to Figure 6.3.6 shows the H₂SO₄ flux of the Dome Fuji, Dome C and NEEM ice cores, respectively. The H₂SO₄ was obtained by subtracting the sulfate-salt concentration from the SO₄²⁻ concentration. For Dome Fuji, there is almost no H₂SO₄ from 25.0–16.0 kyr BP. For 16.0–12.7 kyr BP, the H₂SO₄ has a similar shape as δ¹⁸O of Dome Fuji. The average flux is 0.90 ± 0.66 mg m⁻² yr⁻¹. After 12.7 kyr BP, the flux increased to about a double value (1.84 ± 0.90 mg m⁻² yr⁻¹). The H₂SO₄ flux of Dome C shows almost same fluctuations as Dome Fuji. The average flux for 16.0–12.7 kyr BP is 0.86 ± 0.41 mg m⁻² yr⁻¹, and that after 12.7 kyr BP is 1.53 ± 0.50 mg m⁻² yr⁻¹. For NEEM, the H₂SO₄ flux is seldom found from 26–16.0 kyr BP. After 16.0 kyr BP, the flux increased toward the Holocene. The average flux in the Holocene is 7.03 ± 4.27 mg m⁻² yr⁻¹.

In Antarctica, in general the SO₄²⁻ concentration always exceeds the total cation concentration ([SO₄²⁻] > [Ca²⁺] + [Na⁺] + [NH₄⁺]) when H₂SO₄ is present (Figure 6.3.4b, c and 6.3.5b, c). However, in Greenland, the SO₄²⁻ concentration does not always exceed the total cation concentration when H₂SO₄ is present (Figure 6.3.6b, c). As discussed in Chapter 5, sulfatization of Ca²⁺ and Na⁺ almost fully occurred when [SO₄²⁻] > [Ca²⁺] + [Na⁺] + [NH₄⁺] in Antarctica. On the other hand, in Greenland, sulfatization of Ca²⁺ and Na⁺ does not fully occur due to seasonality and/or transport distance.

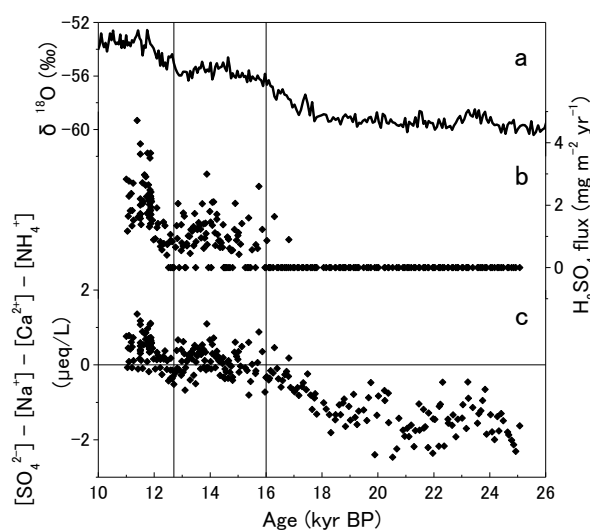


Figure 6.3.4 Temporal variations of H₂SO₄ flux and ionic balance of the Dome Fuji ice core. (a) δ¹⁸O record from Watanabe et al. [2003a]. (b) H₂SO₄ flux. (c) Excess SO₄²⁻ concentration against Na⁺, Ca²⁺ and NH₄⁺ concentrations. Vertical lines indicate 16.0 and 12.7 kyr BP.

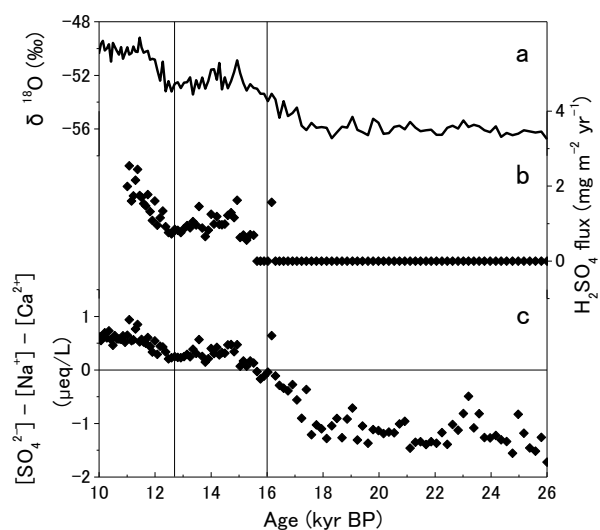


Figure 6.3.5 The same as Figure 6.3.4 except that is shown the Dome C ice core. $\delta^{18}\text{O}$ record from Jouzel et al. [2007]. Vertical lines indicate 16.0 and 12.7 kyr BP.

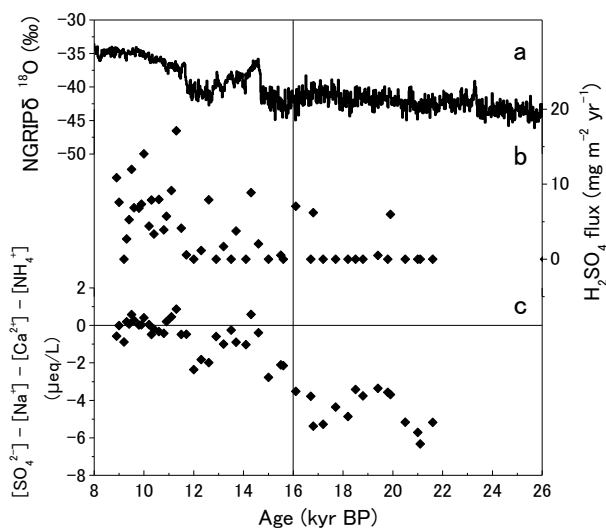


Figure 6.3.6 The same as Figure 6.3.4 except that is shown the NEEM ice core. $\delta^{18}\text{O}$ record from the NGRIP ice core [Rasmussen et al., 2014]. Vertical line marks 16.0 kyr BP.

6.4 Relationship between sulfate-salt flux and temperature changes during the last termination in Greenland and Antarctica

In this section, the changes in the sulfate-salt fluxes in both the Northern and Southern Hemispheres are discussed by comparing them with temperature and other paleoclimate proxies. Then, the contribution of sulfate-salt flux to the last deglacial warming in both polar regions is considered.

6.4.1 Changes in temperature and sulfate-salt flux during the last termination in Greenland

This section discusses the changes in the sulfate-salt flux in Greenland by comparison with temperature and other paleoclimate proxies. In the LGM (around 21 kyr BP), the Greenland temperature was lowest, and the sulfate-salt flux was highest ($17.8 \pm 6.0 \text{ mg m}^{-2} \text{ yr}^{-1}$) in the last termination (Figure 6.4.1a, b). In the LGM, the SO_4^{2-} concentration was high [Legrand et al., 1997]. Also, the source strength and transport efficiency of dust and sea-salt were high, so the concentrations of Ca^{2+} and Na^+ were also high [e.g., Legrand and Mayewski, 1997] (Figure 5.3.2b, c). Due to too high cation concentrations, almost all of SO_4^{2-} was neutralized by cations, and present as sulfate-salt. Therefore, the sulfate-salt flux in the LGM was high.

The last ice recession began in the Northern Hemisphere about 20 kyr BP [Denton et al., 2010], triggered by an increase in summer insolation [Abe-Ouchi et al., 2013]. Massive amounts of fresh water began to be injected in the Atlantic Ocean around 20 kyr BP and reached a maximum between 18.3 and 17.0 kyr BP [Toucanne et al., 2009], which weakened (or shut down) the Atlantic meridional overturning circulation (AMOC) (Figure 6.4.2F) [McManus et al., 2004; Denton et al., 2010]. A weakened AMOC cooled the Northern Hemisphere and warmed the Southern Hemisphere via oceanic and atmospheric teleconnection between around 18 and 14.7 kyr BP [Toggweiler et al., 2008; Barker et al., 2009]. Barker et al. [2009] defined this period of Greenland as Heinrich stadial 1 (HS1) (Figure 6.4.2A). The sulfate-salt flux remained high ($17.6 \pm 5.3 \text{ mg m}^{-2} \text{ yr}^{-1}$) in HS1 (Figure 6.4.1b). Due to the oceanic and atmospheric teleconnection, the Intertropical Convergence Zone (ITCZ) in all ocean basins shifted [Denton et al., 2010]. In the East Asia region, a southward shifted ITCZ weakened the Asian summer monsoon [Okumura et al., 2009]. Due to the weakened Asian monsoon, the Asian region where the major dust source for Greenland ice sheet was located was dry and cold in HS1 (Figure 6.4.2B) [Wang et al., 2001; Ruth et al., 2007]. This dry and cold climate may have increased dust production during this period [Ruth et al., 2007]. In the North Pacific region, the Aleutian low

was strengthened [Okumura et al., 2009]. This strengthened Aleutian low may have strengthened the transport of dust and sea-salt from the Asian and North Pacific regions via the northern branch of the zonal circulation to the Greenland ice sheet [De Angelis et al., 1997]. Source strength and transport efficiency were high, which kept high dust and sea-salt concentrations in Greenland. Like in the LGM, the Ca^{2+} and Na^+ concentrations in HS1 were high (Figure 5.3.2b, c), so most of SO_4^{2-} may have been neutralized by cations and was present as sulfate-salt. As a result, the sulfate-salt flux was high in HS1 (Figure 6.4.1b).

Around 14.7 kyr BP, the AMOC was restored, and the temperature increased to the interstadial climatic stage of Bølling-Allerød (BA) in Greenland (Figure 6.4.2A, F) [McManus, et al., 2004]. The sulfate-salt flux in the BA showed a lower value than that in the LGM and HS1 ($11.4 \pm 5.7 \text{ mg m}^{-2} \text{ yr}^{-1}$) (Figure 6.4.1b). Increased North Atlantic region temperatures instantaneously weakened Asian winter monsoon and strengthened the Asian summer monsoon [Wang et al., 2005]. As a result, the Asian dust region became wet, and the dust production decreased (Figure 6.4.2B) [Wang et al., 2001; Ruth et al., 2007]. Due to the atmospheric teleconnection, the Aleutian low weakened [Wagner et al., 2010]. The source strength of dust and transport efficiency were low, which decreased dust and sea-salt input in Greenland (Figure 5.3.2b, c). As a result, sulfate-salt may have decreased in the BA (Figure 6.4.1b).

Around 13 kyr BP, massive amounts of fresh water were injected into the North Atlantic, and the AMOC reduced again (Figure 6.4.2F) [McManus et al., 2004; Denton et al., 2010]. The climate stage moved to the stadial stage of the Younger Dryas (YD). The sulfate-salt flux increased in the YD compared to the BA ($14.9 \pm 5.8 \text{ mg m}^{-2} \text{ yr}^{-1}$) (Figure 6.4.1b). The situation is similar to the glacial stage. The Asian dust region became cold and dry due to a strengthened Asian winter monsoon (Figure 6.4.2B) [An, 2001; Wang et al., 2001], which increased dust production. Also, the Aleutian low strengthened [Kokorowski et al., 2008]. Similar to the glacial stage, transport of dust and sea-salt were increased in the YD (Figure 5.3.2b, c). Thus, most of SO_4^{2-} may have been neutralized by dust and sea-salt, and was present as sulfate-salt. As a result, the sulfate-salt flux increased in the YD.

At 11.7 kyr BP, Greenland temperatures reached the Holocene level, concomitant with Antarctica. The sulfate-salt flux showed its lowest value in the last termination ($6.8 \pm 3.2 \text{ mg m}^{-2} \text{ yr}^{-1}$) (Figure 6.4.1b). The Asian summer monsoon strengthened, which increased precipitation in the Asian dust source region [Wang et al., 2001; Ruth et al., 2007]. The Aleutian low weakened [De Angelis et al., 1997]. Due to weakened source strength and transport efficiency, the input of dust and sea-salt to Greenland reduced (Figure 5.3.2b, c). Accordingly, the CaSO_4 and Na_2SO_4 flux decreased. On the

other hand, the NH_4^+ became the dominant cation in the Holocene (Figure 5.3.2e). The $(\text{NH}_4)_2\text{SO}_4$ may have been one of the dominant sulfate salts in the Holocene. However, as Figure 6.3.6 shows, not all SO_4^{2-} formed sulfate salts in the Holocene, probably due to seasonality and transport distance as discussed in Chapter 5. The SO_4^{2-} concentration was low in the Holocene; additionally, not all SO_4^{2-} was in the form of sulfate-salt, therefore the sulfate-salt flux showed a low value in the Holocene.

6.4.2 Changes in temperature and sulfate-salt flux during the last termination in Antarctica

This section discusses the changes in the sulfate-salt fluxes in Antarctica. The glacial climate persisted until 18 kyr BP in Antarctica (Phase I in Figure 6.3.1a, b). The temperature was low and the sulfate-salt flux was high. In this period, the dust concentration, which originated mainly from Patagonia, Southern South America [Delmonte et al., 2004, 2008], was particularly high (Figure 5.2.2c). High dust (Ca^{2+}) concentration neutralized almost all SO_4^{2-} , so most of SO_4^{2-} was present as sulfate-salt. As a result, the sulfate-salt flux was high for 25–18 kyr BP (Figure 6.4.1c, d).

Around 18 kyr BP, the AMOC weakened due to injection of massive amounts of fresh water into the Atlantic Ocean (Figure 6.4.2F), which warmed the Southern Hemisphere via oceanic and atmospheric teleconnection. Between 18 and 14.7 kyr BP, the temperature increased (first warming step), while the sulfate-salt flux decreased (Figure 6.4.1c, d). In Southern South America, the Patagonian glaciers receded and the vegetation-covered area increased as a result of the warming [Siani et al., 2010; Sagredo et al., 2011], which suppressed the dust and with it the Ca^{2+} emission [Kaiser and Lamy, 2010]. Indeed, the Ca^{2+} concentration nearly vanished by the end of the first warming around 14.7 kyr BP (Figure 5.2.2c). As a result, neutralization of SO_4^{2-} by Ca^{2+} decreased, then the CaSO_4 production decreased dramatically during this period (Figure 6.3.1e). In the Southern Ocean, southward shifting of the Southern Hemispheric westerlies may have dissipated sea-ice effectively via northward Ekman transport [Anderson et al., 2009]. Due to the reduction of sea-ice extent, the sea-salt (Na^+) emission decreased (Figure 5.2.2b) [Bianchi and Gersonde, 2004; Röthlisberger et al., 2008; Wolff et al., 2010]. The neutralization of SO_4^{2-} by Na^+ also decreased. As a result, not all SO_4^{2-} was in the form of sulfate-salt, then the sulfate-salt flux decreased during the first warming step in Antarctica.

In 14.7–12.7 kyr BP, Antarctica cooled (ACR), which corresponded to the BA in Greenland. The sulfate-salt flux stopped decreasing and stayed at a certain level (Figure 6.4.1c, d). The westerlies and

the Antarctic circumpolar current shifted northward [Denton et al., 2010]. This coupled ocean-atmosphere system transported heat northward, which would stop the rise of sea surface temperature while cooling the air temperature in the Southern Hemisphere [Barker et al., 2009]. Several studies reported that the Patagonian ice sheet advanced in the ACR [Siani et al., 2010; Sagredo et al., 2011]; however, the dust concentration did not increase during this period [Sugden et al., 2009] (Figure 5.2.2c). As a result, neutralization of SO_4^{2-} by Ca^{2+} did not increase, so the CaSO_4 did not increase. On the other hand, the lower sea surface temperature and air temperature would increase the Southern Ocean's sea-ice extent [Bianchi and Gersonde, 2004], which may have increased the sea-salt (Na^+) production. As a result, a certain amount of SO_4^{2-} was neutralized by Na^+ , therefore the sulfate-salt flux stayed at a certain level in ACR.

For 12.7–11.7 kyr BP, Antarctica warmed again (second warming step), which corresponds to the YD in Greenland. The sulfate-salt flux decreased again. During this period, upwelling in the Southern Ocean increased accompanied by a rise in atmospheric CO_2 along with a rapid increase in sea surface temperature [Anderson et al., 2009; Denton et al., 2010] (Figure 6.4.2I, K), which lead to an increase in air temperature and a decrease in sea-ice area. The smaller sea-ice area may then have reduced sea-salt emission (Figure 5.2.2b). As a result, neutralization of SO_4^{2-} by Na^+ decreased, so the sulfate-salt flux decreased in the second warming step in Antarctica.

In the Holocene period (11.7 kyr BP ~), the retreat of the sea-ice area decreased the sulfate-salt flux. Different from Greenland, the contribution of the $(\text{NH}_4)_2\text{SO}_4$ may have been negligibly small, thus the sulfate-salt flux reached a low value in Holocene.

The causes of the sulfate-salt flux changes both in the Northern and Southern Hemispheres have their root in AMOC fluctuation. The production of sulfate-salt was not regulated by SO_4^{2-} , which originates mainly from oceanic phytoplankton, but by physical processes of oceanic and atmospheric systems.

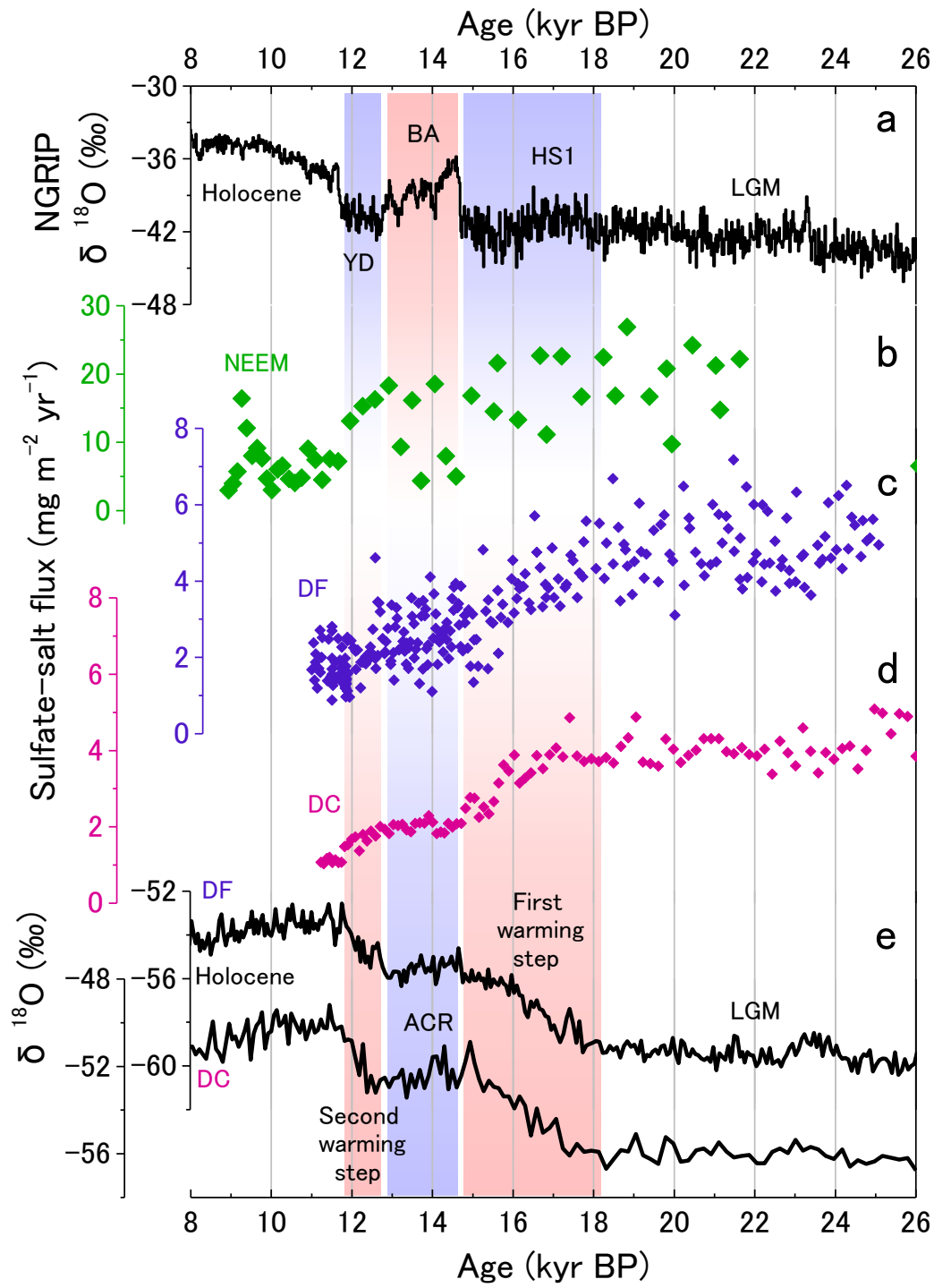


Figure 6.4.1 Temporal variations of sulfate-salt flux of the NEEM, the Dome Fuji, and the Dome C ice cores. (a) $\delta^{18}\text{O}$ record is from the NGRIP ice core [Rasmussen et al., 2014]. (b)–(d) Sulfate-salt flux of the NEEM, the Dome Fuji and the Dome C ice cores (e) $\delta^{18}\text{O}$ of the Dome Fuji ice core [Watanabe et al., 2003a] and that of the Dome C ice core [Jouzel et al., 2007].

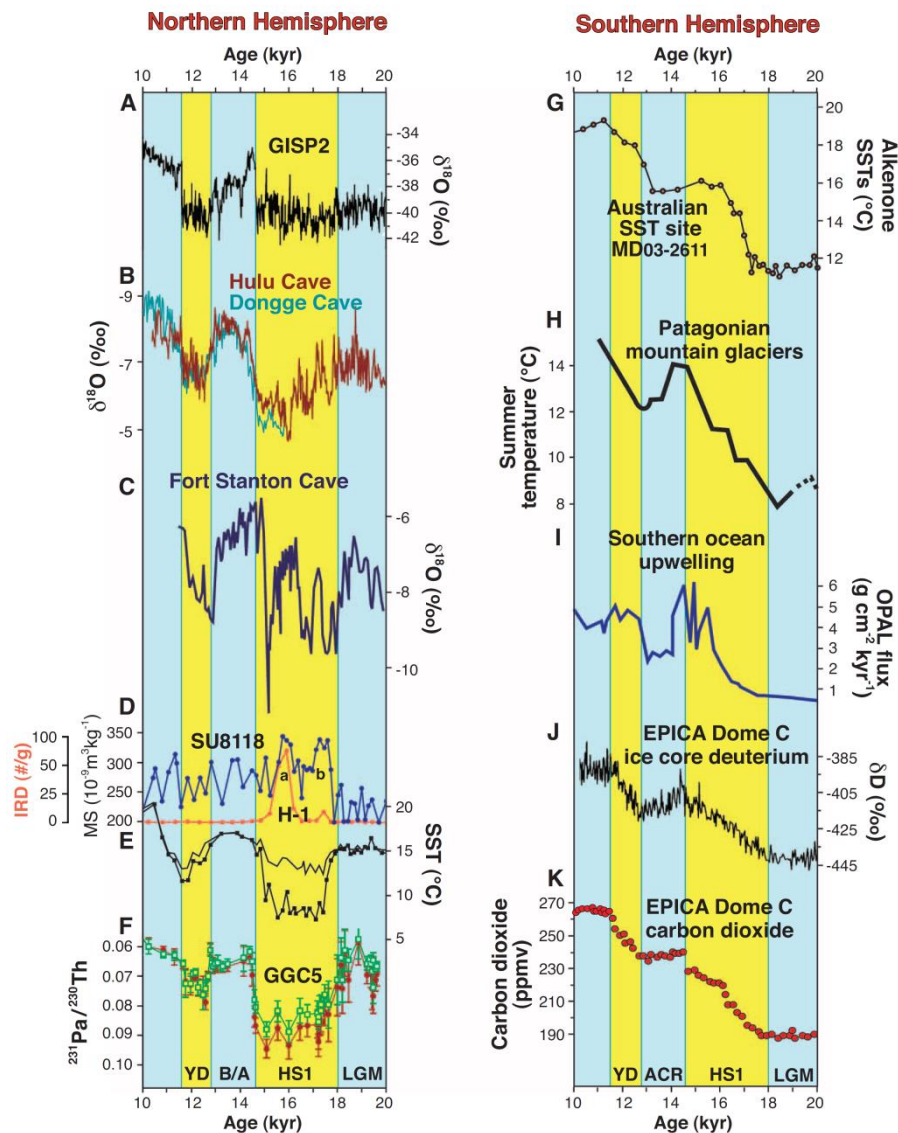


Figure 6.4.2 This figure and caption is obtained from Denton et al. [2010]. (A) GISP2 oxygen isotopes [Stuiver et al., 2000]. (B) Chinese monsoon records reconstructed from speleothems [drier is down, wetter up (Wang et al., 2001; Yuan et al., 2004)]. (C) Precipitation record reconstructed from Fort Stanton Cave, southwestern United States [wetter down, drier up (Asmerom et al., 2010)]. (D) Magnetic susceptibility (MS) and ice-rafted detritus (IRD) from marine sediments located off the coast of Portugal [Bard et al., 2000], where IRD is expressed as the number of grains per gram for the size fraction greater than 150 μm . H-1 is Heinrich Event 1. (E) SST based on alkenone unsaturated ratios from North Atlantic marine sediment core SU-8118 [Bard et al., 2000]. (F) The $^{231}\text{Pa}/^{230}\text{Th}$ ratios from core GGC5 off the Bermuda Rise, where increasing values (plotted downward) reflect reduced Atlantic overturning circulation [McManus et al., 2004]. (G) SST from a site south of Australia ($36^{\circ}44'\text{S}$; $136^{\circ}3'\text{E}$) reconstructed by using the alkenone unsaturation index [Calvo et al., 2007]. (H) Summer temperature changes determined from glacier and vegetation fluctuations in the Andes of Patagonia in southern South America [Denton et al., 1999; Strelin et al., 2005]. (I) Biogenic opal flux in the Southern Ocean, interpreted as a proxy for changes in upwelling south of the Antarctic Polar Front [Anderson et al., 2009]. (J) European Project for Ice Coring in Antarctica (EPICA) Dome C deuterium record [Monnin et al., 2001] as a proxy for temperature in Antarctica. (K) Dome C CO_2 record [Monnin et al., 2001]. EPICA deuterium and CO_2 data are plotted on the GISP2 time scale [after (Marchitto et al., 2007)]. HS1 and the YD are marked with yellow backgrounds, whereas the BA, which is contemporary with the ACR, and LGM have blue backgrounds.

6.4.3 A role of the sulfate-salt flux for the last deglacial warming in both polar regions

The sulfate-salt flux in NEEM is relatively high in Greenland cold climate stages (LGM and YD), whereas the flux is relatively low in Greenland warm climate stages (BA and Holocene) (Figure 6.4.1). In Antarctica, the sulfate-salt flux decreases in Antarctic warming phases (first and second warming step), whereas the flux stops decreasing in Antarctic cooling phases (ACR) (Figure 6.4.1). In this way, the changes in the sulfate-salt flux at each pole are inversely correlated to temperature changes at each pole. A relationship between sulfate-salt flux and water isotope, which is a proxy for temperature, is examined. The squared correlation coefficient of Dome Fuji is $R^2 = 0.71$ ($p < 0.001$), that of Dome C is $R^2 = 0.83$ ($p < 0.001$), and that of NEEM is $R^2 = 0.47$ ($p < 0.001$) (Figure 6.4.3a, c and e). These contrast with the SO_4^{2-} fluxes, which showed no clear correlation with water isotope in all sites (Figure 6.4.3b, d and f). An inverse correlation between sulfate-salt flux and temperature change on the glacial-interglacial time scale has been found for Dome Fuji [Iizuka et al., 2012b]. In this study, I could confirm that this relationship can be seen with higher (350-year) time resolution in the Dome Fuji ice core during the last termination. The same relationship was found in the other site in Antarctica, and also found in the NEEM site, Greenland, with similar time resolution. Sulfate-salt aerosols are a key component of CCN in the atmosphere [Köhler, 1936; Petters and Kreidenweis, 2007], which leads to increased solar scattering that cools Earth's climate [IPCC, 2007, 2013]. Therefore, the reduction in the sulfate-salt flux may have contributed to the last deglacial warming not only in Dome Fuji where a previous study suggested it [Iizuka et al., 2012b], but also in inland Antarctica. Moreover, the inverse correlation between sulfate-salt flux and temperature change in NEEM suggests that sulfate-salt flux may have contributed to the last deglacial warming also in inland Greenland. Results of this study imply that sulfate-salt is one of the considerable climate factors for climate changes in the present and future.

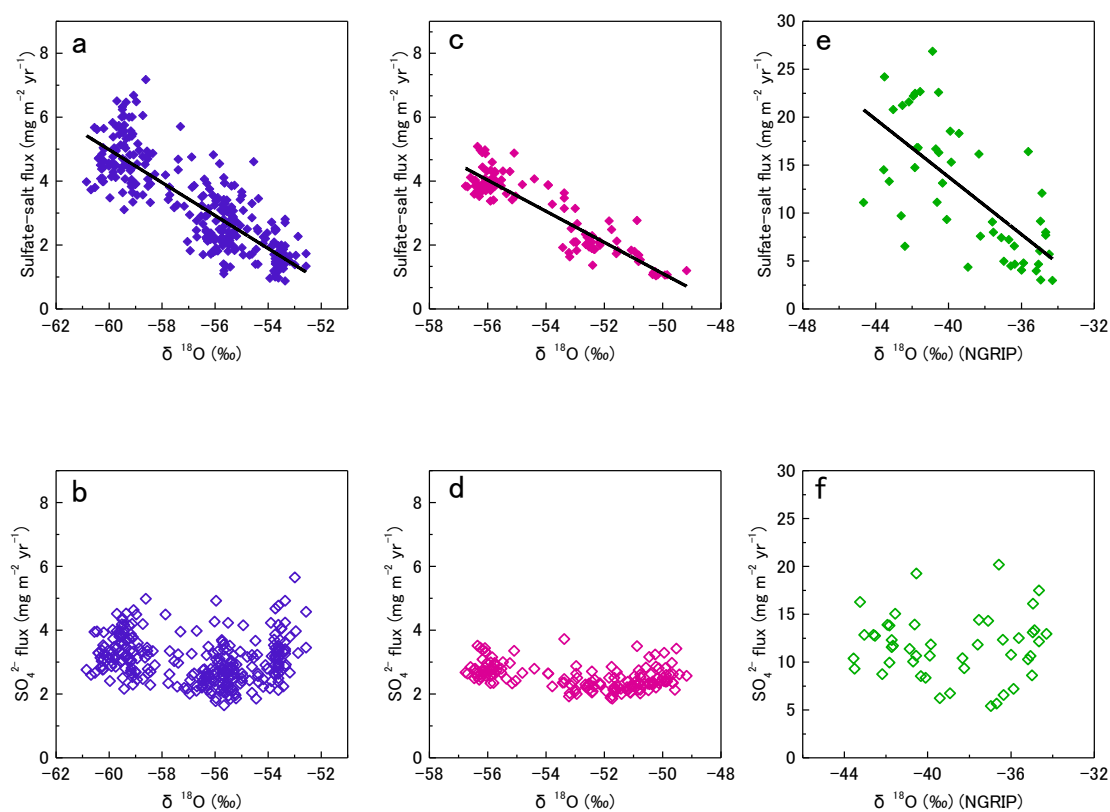


Figure 6.4.3 Correlations of sulfate-salt and SO_4^{2-} fluxes to stable water isotope. Top row is the sulfate-salt flux, and bottom row is SO_4^{2-} flux. (a) and (b) Dome Fuji. The linear fitting line for sulfate-salt is $\text{FSALT} = -0.51 \delta^{18}\text{O} - 25.9$ with $R^2 = 0.71$ ($n = 286$, $p < 0.001$). (c) and (d) Dome C. The linear fitting line for sulfate-salt is $\text{FSALT} = -0.49 \delta^{18}\text{O} - 23.2$ with $R^2 = 0.83$ ($n = 106$, $p < 0.001$). (e) and (f) NEEM. The linear fitting line for sulfate-salt is $\text{FSALT} = -1.50 \delta^{18}\text{O} - 46.2$ with $R^2 = 0.47$ ($n = 43$, $p < 0.001$). $\delta^{18}\text{O}$ record is from the NGRIP ice core [Rasmussen et al., 2014].

CHAPTER 7

7 Summary

This chapter summarises the main achievements of this research. Using the ice-sublimation method, chemical compositions of non-volatile particles preserved in the Dome Fuji, Dome C and NEEM ice cores were analysed. This study clarified the major components of soluble salt particles and their time series variations during the last termination in the Dome Fuji, Dome C and NEEM ice cores. Also, this study constructed the new ion-deduced methods for the Antarctic ice cores and the Greenland ice cores, and estimated salts concentrations in the Dome Fuji, Dome C and NEEM ice cores. These achievements are new knowledge for the interpretation of ice core records and for the clarification of the role of the soluble aerosols for climate changes, which have not been obtained by traditional ice core studies of soluble aerosols (ion concentrations).

7.1 The major compositions of soluble salt particles in the Antarctic ice cores

The major components of soluble salt particles during the last termination in the Dome Fuji and Dome C ice cores are the same to each other. The major components of soluble salt particles of the Dome Fuji and Dome C ice cores are CaSO_4 , Na_2SO_4 and NaCl (section 3.2). From 25 to 18 kyr BP, the CaSO_4 and NaCl fractions are high and the Na_2SO_4 fraction is low. Between 18 and 16 kyr BP, the CaSO_4 and NaCl fractions decreased and the Na_2SO_4 fraction increased. During 16–11.7 kyr BP, the CaSO_4 and NaCl fractions are low and Na_2SO_4 fraction is high (Section 3.4, 5.1).

The main cause of these changes is the decrease in the Ca^{2+} concentration from the LGM to the Holocene. During 25–18 kyr BP, most of the Ca^{2+} forms CaSO_4 but some of Na^+ remained as NaCl because Ca^{2+} was sulfatized prior to Na^+ , and Ca^{2+} concentration was high. As a result, the CaSO_4 and NaCl fractions were high in this period. Between 18–16 kyr BP, the Ca^{2+} concentration decreased dramatically. Accordingly, NaCl sulfatization increased. As a result, CaSO_4 and NaCl fractions

decreased and the Na_2SO_4 fraction increased in this period. During 16–11.7 kyr BP, the contribution of Ca^{2+} was low and the Na^+ became dominant. In this period, the SO_4^{2-} concentration exceeded the sum of the Ca^{2+} and Na^+ concentrations. As a result, most of NaCl sulfatized to Na_2SO_4 , and the Na_2SO_4 fraction was high during 16–11.7 kyr BP (section 5.2). Between 12.3 and 9.6 kyr BP in Dome Fuji, and between 9.5 and 7.5 kyr BP in Dome C, the NaCl/ Na_2SO_4 ratio showed a high value. This high NaCl/ Na_2SO_4 variability is likely linked to an increase in the seasonal contribution of NaCl to the atmospheric aerosol in winter during the period (section 4.1).

Using the new ion-deduced method, which takes into account seasonality, the CaSO_4 , Na_2SO_4 and NaCl fluxes were calculated (sections 6.1 and 6.3). These fluxes in the Dome Fuji ice core are similar to those in the Dome C ice core. The CaSO_4 and NaCl fluxes decreased from the LGM to the Holocene, whereas the Na_2SO_4 flux did not decrease from the LGM to the Holocene.

7.2 The major compositions of soluble salt particles in the Greenland ice core

The major components of soluble salt particles over a glacial-interglacial cycle in the NEEM ice core were NaCl, Na_2SO_4 , CaSO_4 and other-Ca (CaCO_3 in glacial period) (section 3.2). From differences of the fractions of Ca-salt and Na-salt, 7 climatic stages can be sorted into three groups; Interglacial-group (Holocene and Stratigraphic Disruptions Section), Bølling-Allerød (medium stage between interglacial-group and glacial group in terms of a temperature), and Glacial-group (Younger Dryas, LGM, DO events-warm and DO events-cold). In the Interglacial-group, Na-salt accounts for about 50% of total soluble particles, whereas Ca-salt accounts for more than 50% of total soluble particles in the Glacial-group. Different from the Holocene and Glacial-group, the BA record shows that the number ratio of Ca-salt to Na-salt is close to 1. Moreover, the Glacial-group was divided into mild-type (YD & DO-w) and cold-type (LGM & DO-c). The fraction of CaSO_4 was higher in mild-type than that in cold-type (section 3.5).

Focusing on the last termination, the soluble salt composition in the LGM is characterized by high Ca-salt with high CaCO_3 fraction. In the BA, the CaCO_3 fraction decreased, instead the NaCl and Na_2SO_4 fractions increased. In the YD, the fractions of CaCO_3 and CaSO_4 increased, whereas those of NaCl and Na_2SO_4 decreased. The CaSO_4 fraction was especially high in YD. In the Holocene, the fractions of CaCO_3 and CaSO_4 decreased, instead those of NaCl and Na_2SO_4 increased (section 3.5 and 5.1).

These changes are mainly controlled by the Ca^{2+} concentration. In the LGM, due to too high Ca^{2+} concentration, most of SO_4^{2-} was consumed by Ca^{2+} . The excess Ca^{2+} concentration against SO_4^{2-} concentration was in the form of CaCO_3 . As a result, the CaCO_3 fraction was high in the LGM. In the BA, the contribution of Ca^{2+} became low. Accordingly, the contribution of Na^+ and NaCl sulfatization increased. As a result, the NaCl and Na_2SO_4 fractions increased in the BA. In the YD, the contribution of Ca^{2+} increased again. However, different from the LGM, the Ca^{2+} concentration is low against SO_4^{2-} concentration. As a result, Ca^{2+} sulfatization in the YD was more efficiently than in the LGM, therefore the CaSO_4 fraction was high in the YD. In the Holocene, the contribution of Ca^{2+} became low. Accordingly, the contribution of Na^+ and NaCl sulfatization increased, so the NaCl and Na_2SO_4 fractions increased. However, despite the SO_4^{2-} concentration is higher than the sum of Ca^{2+} and Na^+ concentrations as well as in Antarctica, more than half of Na-salt exists as NaCl. Due to increase of NH_4^+ , different seasonal variations of Na^+ and SO_4^{2-} , and/or meteorological conditions and site location of NEEM, some of Na^+ was in the form of NaCl in the Holocene (section 5.3).

Using molar ratios that result from the sublimation method, the CaCO_3 , CaSO_4 , NaCl and Na_2SO_4 fluxes were calculated (sections 6.2 and 6.3). These absolute fluxes of the NEEM ice core were higher than those of the Dome Fuji and Dome C ice cores. The CaCO_3 , CaSO_4 and NaCl fluxes decreased from the LGM to the Holocene, whereas the Na_2SO_4 flux did not decrease from the LGM to the Holocene. The reduction rate of the CaSO_4 flux from the LGM to the Holocene in the NEEM ice core was larger than in the Dome Fuji and Dome C ice cores, whereas that of Na_2SO_4 flux was similar in the three ice cores.

7.3 Bipolar sulfate-salt flux and temperature changes during the last termination

Using ion-deduced methods for the Greenland and Antarctic ice cores, the sulfate-salt fluxes of the NEEM, Dome Fuji and Dome C ice cores were calculated (sections 6.1 and 6.2). The sulfate-salt flux in the NEEM ice core is relatively high during Greenland cold climate stages (LGM and YD), whereas the flux is relatively low during Greenland warm climate stages (BA and Holocene). In Antarctica, the sulfate-salt flux decreases during Antarctic warming phases (first and second warming step), whereas the flux stops decreasing during Antarctic cooling phases (ACR). In this way, the changes in the sulfate-salt flux at each pole correspond to temperature changes at each pole. The sulfate-salt flux of

all three cores has a significant inverse correlation with temperature changes in each site with several hundred years time resolution. This contrasts with the SO_4^{2-} flux, which showed no clear correlation with temperature at all sites. In this way, inverse correlations between sulfate-salt fluxes and temperature changes could be found by separating the SO_4^{2-} into sulfate salts and acid using the ice-sublimation method.

The sulfate-salt flux changes in both hemispheres are caused by the Atlantic Meridional Overturning Circulation fluctuations. The production of sulfate-salt was regulated not by SO_4^{2-} , which is mainly from oceanic phytoplankton, but by physical processes of oceanic and atmospheric systems. Sulfate-salt aerosols are a key component of CCN in the atmosphere, which leads to increased solar scattering that cools Earth's climate. The reduction in the sulfate-salt flux, therefore, may have contributed to the last deglacial warming not only in Dome Fuji where a previous study suggested it but also in inland Antarctica. Moreover, the inverse correlation between sulfate-salt flux and temperature change in the NEEM ice core suggests that sulfate-salt flux may have contributed to the last deglacial warming both in inland Antarctica and Greenland (sections 6.3 and 6.4).

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