Horizontal distributions of aerosol constituents and their mixing states in Antarctica during the JASE traverse

K. Hara[1], F. Nakazawa[2], S. Fujita[2], K. Fukui[2, now at 3], H. Enomoto[4, now at 2], and S. Sugiyama[5]

1: Department of Earth System Science, Faculty of Science, Fukuoka University, Fukuoka, Japan

2: National Institute of Polar Research, Tokyo, Japan

3: Tateyama Caldera Sabo Museum, Toyama, Japan

4: Kitami Institute of Technology, Kitami, Japan

5: Institute of Low temperature Science, Hokkaido University, Sapporo, Japan

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Abstract

Measurements of aerosol number concentrations and direct aerosol sampling were conducted on continental Antarctica during the traverse of the Japanese–Swedish joint Antarctic expedition (JASE) from 14 November 2007 until 24 January 2008. Aerosol concentrations in background conditions decreased gradually with latitude in inland regions during the traverse. The lowest aerosol number concentrations were 160 L^{-1} in $D_p > 0.3$ μm, and 0.5 L^{-1} in $D_p > 2$ μm. In contrast, aerosol concentrations reached 3278 L^{-1} in $D_p > 0.3$ μm, and 215 L^{-1} in $D_p > 2$ μm under strong wind conditions. The estimated aerosol mass concentrations were 0.04–5.7 μg m^{-3}. Single particle analysis of aerosol particles collected during the JASE traverse was conducted using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer. Major aerosol constituents were sulfates in fine mode, and sulfate, sea-salts, modified sea-salts, and fractionated sea-salts in coarse mode. K-rich sulfates, Mg-rich sulfate, Ca-rich sulfates, and minerals were identified as minor aerosol constituents. Horizontal features of Cl/Na ratios imply that sea-salt modification (i.e. Cl loss) occurred on the Antarctic continent during the summer. Most sea-salt particles in the continental region near the coast were modified with acidic sulfur species such as H_2SO_4 and CH_3SO_3H. By contrast, acidic species other than the acidic sulfur species (likely HNO_3) contributed markedly to sea-salt modification in inland areas during the traverse. Mg-rich sea-salt particles and Mg-free sea-salt particles were present in coarse and fine modes from the

coast to inland areas. These sea-salt particles might be associated with sea-salt fractionation on the snow surface of continental Antarctica.

1 Introduction

Atmospheric aerosol constituents in Antarctic regions have been measured for more than three decades to elucidate the regions' aerosol chemistry, to monitor Earth background levels, and to interpret ice core records (Savoie et al., 1992, 1993; Minikin et al., 1998; Legrand et al., 2001; Hara et al., 2004; Weller et al., 2011). Although most investigations of aerosol chemistry have been conducted at coastal stations such as Syowa Station, Neumayer Station, Halley Station, Dumont d'Urville Station, and Mawson Station (Savoie et al., 1992, 1993; Legrand et al., 2001; Hara et al., 2004; Weller et al., 2011), aerosol chemistry and atmospheric chemistry have been investigated recently even at inland stations such as Amundsen–Scott (South Pole) Station, Dome F Station, Kohnen Station, and Concordia (Dome C) Station (Bodhaine, 1995; Hara et al., 2004; Weller and Wagenbach, 2007; Jourdain et al., 2008; Eisele et al., 2008; Udisti et al., 2012).

From those earlier investigations, basic aerosol chemical properties were obtained: seasonal features of the concentrations of major aerosol constituents (SO_4^{2-}, $CH_3SO_3^-$, NO_3^-, and sea-salts (e.g., Na^+ and Cl^-)), and minor aerosol constituents (minerals and carbonaceous species (soot and organics)) at Antarctic coasts and inland area. In those investigations, aerosol constituents were determined using bulk analysis techniques (mainly ion chromatography). Such techniques, however, cannot provide sufficient information about the mixing states of respective aerosol constituents. That information is necessary to elucidate the origins of constituents and the chemical reactions that occur on aerosol particles (heterogeneous reactions). For sample analysis, single particle analysis takes longer than bulk analysis. Therefore, few previous investigations have used single particle analysis (Parungo et al., 1979; Yamato et al., 1987a, 1987b; Artaxo et al., 1992; Mouri et al., 1999; Hara et al., 1996, 2005, 2013).

Previous investigations (e.g., Savoie et al., 1992, 1993; Minikin et al., 1998; Hara et al., 2004, 2013) showed that major aerosol constituents in Antarctic atmosphere near surface were sulfates (probably H_2SO_4) in summer and sea-salts in winter–spring. Actually, SO_4^{2-} and $CH_3SO_3^-$ are strongly dominant during the summer on the Antarctica because of biogenic activity in the ocean (e.g., Minikin et al., 1998; Legrand et al., 2001). Size segregated aerosol analysis showed that SO_4^{2-} and $CH_3SO_3^-$ were distributed mainly in the sub-micrometer range at the Antarctic coasts (e.g., Jourdain and Legrand, 2001; Read et al., 2008). Yamato et al. (1987a, 1987b) used chemical testing (Ca thin-film method) to demonstrate that sulfuric acid was dominant in aerosol constituents in Antarctic troposphere during summer. In addition, single particle analysis using laser microprobe mass spectrometry showed that $CH_3SO_3^-$ was mixed internally with sulfate particles (probably H_2SO_4 particles) near the surface on the Antarctic coasts during summer (Wouters et al., 1990; Hara et al., 1995).

Sea-salts are dominant during winter–spring (e.g., Hara et al., 2004). Sea-salt particles were distributed widely in ultrafine–coarse mode throughout the year at Syowa Station (Hara et al., 2010a, 2011a) and were distributed in fine–coarse mode during the summer at Aboa Station (Kerminen et al., 2000; Teinilä et al., 2000). From elemental analysis of individual particles using EDX, Mouri et al. (1999) and Hara et al. (2005, 2013) reported that sea-salt particles near the surface were modified with SO_4^{2-} and $CH_3SO_3^-$ during the summer, and were modified with NO_3^- in August at Syowa Station. Furthermore, single particle analysis of aerosol particles collected using tethered-balloon operations exhibited seasonal and vertical features of aerosol constituents and their mixing states in near surface – lower free troposphere (2.5 km), sea-salt modification, and sea-salt fractionation (Hara et al., 2013). In addition to sea-salt modification, sea-salt particles were fractionated through precipitation of several salts such as mirabilite (Na_2SO_4 $10H_2O$) and hydrohalite (NaCl $2H_2O$) in sea ice formation and frost flower appearance under colder conditions (e.g., Wagenbach et al., 1998; Rankin et al., 2000, 2002; Hara et al., 2004, 2012). Sea-salt fractionation on sea ice (including frost flowers) by depletion of Na-salts engenders Mg-enrichment in sea-salt particles during winter–spring on the Antarctic coast (Hara et al., 2010, 2012, 2013). Furthermore, Hara et al. (2013) pointed out the likelihood that sea-salt fractionation (Mg separation in sea-salt particles) occurs during summer. The following questions, however, remain; (1) “Where does sea-salt fractionation occur on the Antarctic regions during summer?”, and (2) “What are the specific processes of sea-salt fractionation (Mg separation)?”.

Although useful and important knowledge related to aerosol chemical properties (e.g., concentrations, and mixing states) has been obtained gradually from previous investigations using bulk and single-particle analysis of aerosol particles along the Antarctic coasts, a great dearth of knowledge remains for aerosol chemical properties and chemical processes taking place on the Antarctic continent. To elucidate spatiotemporal features of glaciological environment and atmospheric quality in Droning Maud Land, East Antarctica, scientific traverse using snow vehicles was conducted by a Japanese Swedish Antarctic Expedition (JASE) in the austral summer of 2007/2008 (Fujita et al., 2011). In this study, measurements of the aerosol number concentrations and direct aerosol sampling were conducted during the JASE traverse to characterize and elucidate the horizontal features of aerosol constituents and their mixing states in the atmosphere near the ground on the Antarctic continent during summer. Herein, we mainly discuss (1) the horizontal distributions of aerosol constituents and mixing states on the Antarctic continent during summer, (2) sea-salt modification, and (3) sea-salt fractionation.

2 Aerosol measurements and data analysis

2-1 JASE traverse

Figure 1 depicts the JASE traverse route in Droning Maud Land, East Antarctica. On this campaign, the Japanese team traveled from S16 on the Antarctic continent (near Syowa Station) to a meeting point on the Antarctic plateau via Dome F Station. The Swedish team traveled from Wasa Station to the meeting point via Kohnen Station. Aerosol measurements and direct aerosol sampling for this study were conducted during the Japanese team traverse. The Japanese traverse team left from S16 on 14 November 2007, and arrived at the meeting point on 27 December 2007 in the incoming traverse. After some joint scientific work at the meeting point conducted for several days, the outgoing traverse (return to S16) began on 30 December 2007. During the outgoing traverse, the Japanese team traveled from the meeting point to Dome F on the southern side of the ice divide for glaciological measurements. The team approached S16 on 24 January 2008. Details of the traverse were described by Fujita et al. (2011).

2-2 Meteorological measurements during the JASE traverse

Continuous measurements of air pressure (F4711; Yokogawa Analytical Systems Inc.), air temperature (KDC-A01-S001 and KADEC21-U4; Kona System Inc.), wind speed, and wind direction (KADEC21-KAZE; Kona System Inc.) were performed during the JASE traverse. Meteorological sensors were fixed on the snow vehicle, located approximately at 3 m above the snow surface. Daily meteorological observations (air, pressure, air temperature, wind direction, wind speed, weather, visibility, degree of cloud cover, and cloud type) were made around 15:00 LT. Weather conditions were observed also during aerosol measurements conducted at camp sites.

2-3 Aerosol measurements

Aerosol measurements and direct aerosol sampling were conducted during the JASE traverse. For safe operation of aerosol measurements, measurements of the aerosol size distribution, and direct aerosol sampling were not made during the traverse during the daytime but were conducted only at camp sites.

2-3-1 Measurements of aerosol number concentrations

Aerosol number concentrations were measured using a portable optical particle counter (OPC, KR12A; Rion Co. Ltd.) during direct aerosol sampling at every camp site. The measurable size range was $D_p > 0.3$, 0.5, 0.7, 1.0, 2.0, and 5.0 μm. The OPC was calibrated using spherical polystyrene latex particles with refractive index of 1.59–0i. Consequently, the size provided from OPC is “optically PSL-equivalent size”. The OPC packed in an insulator box was set at ca. 1 m above the snow surface by tripod, located on the windward side of the camp site to avoid local contamination (mainly exhaust from snow vehicles). Aerosol number concentrations were recorded with resolution of every 23–25 s (corresponding to 1 liter air sucking) during direct aerosol sampling. The ambient number concentrations were converted to concentration under standard conditions (0 °C and 1013.25 hPa).

2-3-2 Direct aerosol sampling and analysis

Aerosol particles were collected on carbon-coated collodion thin film supported by Ni-microgrid (square-300 mesh; Veco Co.) using a two-stage aerosol impactor. The cut-off diameters of the impactor were 2.0 and 0.2 μm in aerodynamic diameter at a flow rate of 1 liter min^{-1}. The aerodynamic diameter was estimated for particles density of 1 g cm^{-3}. The aerosol particle density, however, is mostly larger than 1 g cm^{-3}, for instance, NaCl (2.2 g cm^{-3}), and H_2SO_4 (1.84 g cm^{-3}). Therefore, aerosol particles slightly smaller than the cut-off diameter (aerodynamic diameter) can be collected on the sample substrates, depending on the particle density. The impactor was set at ca. 1 m above the snow surface next the OPC. Because of the lower aerosol number concentrations on the Antarctic continent, direct aerosol sampling was conducted for 28–86 min (mean, 60 min) depending on the aerosol number concentration. After direct sampling, aerosol samples were kept in air tight boxes including desiccant until analysis in our laboratory in Japan to avoid humidification that can engender morphological change, modification (chemical reactions), and fractionation, as described by Hara et al. (2002, 2005, 2013). Therefore, aerosol modification and fractionation might be negligible, although aerosol constituents can be solidified separately in each aerosol particle because of efflorescence of deliquescent aerosol particles under dry conditions.

Individual aerosol particles on the sample substrate were observed and analyzed in this study using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDX; Quanta FEG-200F, FEI; XL30; EDAX Inc.). Analytical conditions were the following: 20 kV accelerating voltage and 30 s counting time. To avoid analytical bias of localization of aerosol constituents in each particle, the rectangular or square area almost covering a particle was scanned using an electron beam in EDX analysis. The analytical depth in SEM-EDX analysis depends on the accelerating voltage, chemical composition, density, and other factors. Although secondary electrons can be emitted from a depth of several ~ 10 nm (e.g., Ding et al., 2009), characteristic X-rays can be emitted from a depth of a few μm (e.g., Goldstein *et al.* 2007). Most of the coarse particles examined in this study were smaller than 3 μm in diameter. Consequently, characteristic X-rays were obtained from whole particle in fine and coarse mode in this study. When the particle thickness is larger than ca. 5 μm, compositions near surface (thickness of a few micrometers) might be detected. However, only a few particles larger than 5 μm were found in a single sample. Details of analytical procedures and data quality were described by Hara et al. (2002, 2005, 2013). We analyzed 2690 particles in coarse mode (mean: 58 particles / sample) and 45,044 particles in fine mode (mean: 961 particles / sample). Most aerosol-sampled areas on the substrates were analyzed in coarse mode in this study. Although we attempted to analyze as many coarse particles as possible, the lower aerosol number concentrations in coarse mode limit the number of the analyzed aerosol particles in this study. However, 20–30% of the aerosol-sampled area on the substrates was analyzed in aerosol samples in fine mode.

3 Results and Discussion

3-1 Meteorological conditions during the JASE campaign

3-1-2 Air temperature, wind speed, and weather near the surface

Figure 2 shows variations of latitude, elevation, air temperature, and wind speed during the JASE traverse of the Japanese team. The air temperature decreased gradually with latitude in 69−73 °S in both the incoming and outgoing traverse, although the highest temperature near the coast was ca. -7.6 °C in the incoming traverse and -2.9 °C in the outgoing traverse. By contrast, the air temperature was around -30 °C at latitudes higher than 73 °S in this study. The lowest air temperature was -43 °C. In addition, air temperature showed strong diurnal variation. The diurnal temperature range was approximately 8.6 °C on average (maximum, 16 °C).

Wind speed often showed diurnal features during the traverse. In addition to diurnal features of wind speed, the wind speed increased because of an approaching cyclone, for example on 18−22 November, 27−30 November, 7–8 December, and 20−23 December. Although the diurnal maximum of air temperature was observed at noon time (LT), those of wind speed were lagged at latitudes lower than 73 °S. Similarly, similar diurnal variations of wind speed were observed on Antarctic continent (Allison, 1998; Van As et al., 2005) and Antarctic coasts (Sato and Hirasawa, 2007). However, the diurnal maxima of wind speed were mutually synchronized well to those of air temperature at latitudes higher than 74 °S, when their diurnal features occur. According to a manual weather check at every camp site, the weather was mostly clear and fine. When the wind speed was greater than ca. 6 m s^{-1}, drifting snow prevailed during the traverse, for example on 28–29 November, 7 December, and 21–23 December.

3-1-2 Air mass history during the JASE traverse

To elucidate the history and origins of air masses observed in this study, the 5-day backward trajectory was computed using the NCEP reanalysis dataset and vertical motion mode in this study (Draxler and Rolph, 2013). Uncertainty of the trajectory analysis derives from the resolution of meteorological data (wind field), calculation scheme, and trajectory model. Kahl et al. (1989) and Stohl et al. (1995) reported that error reached hundreds ~1000 km after trajectory calculation for 5 days. Therefore, the 5-day backward trajectory was analyzed in this study. Indeed, previous works (Reijmer et al., 2001, 2002; Hara et al., 2004, 2013; Suzuki et al., 2008) used 5-day backward trajectory analysis to elucidate the origins of moisture and aerosols. In general, uncertainty can be greater when the starting altitude of trajectories is within in boundary layer. The 5-day backward trajectories from altitudes in the boundary layer – free troposphere, however, were closely consistent well with vertical profiles of aerosol constituents over Syowa Station, Antarctica (Hara et al., 2013). For the present study, we calculated the trajectories from 200, 500, and 1000 m above ground level. The trajectories showed similar vertical features and transport pathways in most cases, so that a 5-day backward trajectory might be applied to discuss air mass history even in the Antarctic continent.

Figure 3 depicts backward trajectories from 200 m above ground level over each camp site. As depicted in Fig. 3a, air masses from the camp sites located in 69–71 °S in the incoming traverse were transported westward along with Antarctic coastal line during the prior 5 days. Vertical features of the backward trajectories imply that these air masses traveled in the upper boundary and lower free troposphere. In contrast to the transport pathway in 69–71 °S, air masses at the camp sites in >71 °S traveled in the free troposphere over the Antarctic continent during the prior 5 days. Air masses in the traverse from Dome F to the meeting point flowed over the Antarctic plateau during the prior 5 days (Fig. 3b). The vertical motions in these air masses were classified into (1) transport from the free troposphere and (2) travel in the boundary layer (near surface). Compared to the weather at camp sites, the first type (transport from free troposphere) and second type (transport in the boundary layer) corresponded to days with good weather, and to days with strong winds and drifting snow conditions. Backward trajectories in the outgoing traverse from the meeting point to Dome F indicate transport in the boundary layer – lower free troposphere over the Antarctic continent (Fig. 3c). The transport pathway during the outgoing traverse from Dome F to S16 was clearly divisible into transport from coastal areas and transport over the continent (Fig. 3c). Although air masses at latitudes higher than 73 °S traveled over the continent, air masses at >75 °S and at 73–75 °S were transported from near the South Pole, and were transported along ice ridges through near Dome A and Dome C in East Antarctica. Furthermore, air masses in the outgoing traverse moved near ground level (probably in the boundary layer) for the past 5 days, in contrast to the large variation of vertical motions in the incoming traverse from S16 to Dome F. These features of transport pathways of air masses on the Antarctic continent during the JASE traverse showed good agreement with seasonal variations of the air mass origins and transport pathway over the Antarctic continent by Suzuki et al. (2013).

3-2 Number concentrations, mass concentrations, and size distribution of aerosol particles during the JASE traverse

Figures 4 and 5 depict features of wind speed, the aerosol number concentrations, Junge slope, and aerosol mass concentrations during direct aerosol sampling at each camp site during the JASE traverse. During the incoming traverse, the aerosol number concentrations decreased gradually with latitude and elevation, except high number concentrations in strong winds. Higher aerosol number concentrations were identified under conditions with wind speeds higher than 6 m s^{-1} in this study. Therefore, we use aerosol concentrations at wind speeds lower than 6 m s^{-1} as “background aerosol concentrations” in this study. For instance, the background number concentrations in D_p >0.3 μm and D_p >2 μm changed, respectively, from ca. 1330 L^{-1} near the coast to ca. 160 L^{-1}, and from 36 L^{-1} to 0.5 L^{-1}. The number concentrations on the Antarctic continent during the JASE traverse were lower than those in the lower free troposphere over Syowa Station in summer (Hara et al., 2011b). The aerosol number concentrations increased considerably under strong wind and drifting snow conditions. Considering that air masses on the Antarctic continent during JASE were not transported from coastal areas during the prior 5 days, this increase suggests that strong winds engender the release of aerosol particles and small snow/ice flakes from the snow surface. Particularly the number concentrations in coarse particles having diameter larger than 2.0 μm increased remarkably by 1–2 orders of magnitude higher in strong wind conditions, as shown in Figs. 4 and 5. The aerosol number concentrations and their horizontal features in the outgoing traverse were similar to those in the incoming traverse.

For comparison of the aerosol size distribution, we estimated the “Junge-slope” in this study. The aerosol size distribution in fine–coarse mode can be approximated as the following equation (Junge, 1963).

$$\frac{\mathrm{dN}}{\mathrm{dlogD_p}} = \alpha D_p^{-\beta}$$

Therein, α and β respectively represent a constant and the Junge-slope. The Junge slope is often used as an index of the shape of aerosol size distribution in fine–coarse modes. For instance, higher (lower) Junge-slope values are visible, respectively, in cases of high (low) number concentrations in fine mode and/or low (high) concentrations in coarse mode, respectively. In this study, the Junge slope (β) was estimated as 0.3–5.0 μm in diameter. The Junge slope was 2.22–3.03 (mean, 2.70; median, 2.75) in background conditions (wind speed lower than 6 m s^{-1}) in the incoming traverse. In contrast, the Junge slope decreased to less than 2.5 under conditions with strong winds (>6 m s^{-1}) or drifting snow. The Junge slope in the outgoing traverse was 2.73–3.37 (mean, 3.03; median, 2.92) under background conditions. Similar to the Junge slope in the incoming traverse, the Junge slope decreased in strong winds during the outgoing traverse. The considerable decrease of June slope in strong wind corresponded to high number concentrations in coarse mode (Figs. 4-5). Consequently, aerosol size distributions depended closely on release of aerosol particles from snow surfaces by blowing winds. In addition, the Junge slopes in the outgoing traverse were slightly larger than those in the incoming traverse. This difference derived from the reduction of aerosol release (especially in coarse mode) from the snow surface under calm wind conditions during the outgoing traverse. Considering that weather conditions are usually stable in December–January on the Antarctic region (e.g., Sato and Hirasawa, 2007), these differences between the incoming traverse and outgoing traverse might reflect seasonal features of aerosol number concentrations and the size distribution on the Antarctic continent during early summer (or end-spring) through mid-summer. Compared to the Junge slope in the lower troposphere over Syowa Station during the summer (range, 2.2–3.2; median, 2.5; Hara et al., 2011b), the Junge slope was slightly greater on the Antarctic continent during the JASE traverse. The difference of the Junge slopes might result from horizontal features of the number concentrations, particularly in coarse mode, from coasts to inland areas. Indeed, the number concentrations in coarse mode in JASE traverse were several factors – one order lower than those over Syowa Station.

Here, we attempt to estimate the mass concentrations using aerosol number concentrations measured with OPC. The spherical shape and density were assumed in the estimation. As described above, diameters in OPC are the “optically PSL-equivalent size”, so that the estimated aerosol volume means “PSL-equivalent volume” in this study. The densities corresponded to those of sulfates (ca. 1.8 g cm^{-3}) and NaCl (2.2 g cm^{-3}). Major aerosol constituents were sulfate particles during JASE traverse (details are presented later herein). Therefore, we used the density of 1.8 g cm^{-3} to estimate the mass concentration in this study. The number concentrations of aerosol particles smaller than 0.3 µm were not included in the estimation. Therefore, the estimated mass concentrations can be slightly underestimated. In addition, the aerosol number concentrations were observed using OPC above the snow surface. Consequently, the number concentrations were measured under ambient conditions (not dry conditions), although OPC had been packed in an insulator box. Therefore, the estimated mass concentrations included masses of water in aerosol particles in this study. The presence of water in aerosol particles can cause overestimation of the aerosol density and mass concentrations because of salt dilution by water.

With the exception of higher mass concentrations under conditions with drifting snow and strong winds, the aerosol mass concentrations decreased gradually from ca. 0.16 µg m^{-3} (near the coasts) to 0.04 µg m^{-3} (near Dome F Station). The mass concentrations on the Antarctic continent during JASE traverse were similar to the mass concentrations of water soluble aerosol constituents at Kohnen Station (Weller and Wagenbach, 2007).

They were slightly higher than the mass concentrations water soluble aerosol constituents at Dome C (Preunkert et al., 2008; Udisti et al., 2010). The aerosol mass concentrations increased considerably to greater than several micrograms per cubic meter under conditions with drifting snow and strong winds. The highest mass concentrations were approximately 5.7 μg m^{-3}. Higher mass concentrations were observed in high number concentrations in coarse mode. Therefore, aerosol particles from the snow surface by erosion under strong winds might make a substantial contribution to high aerosol mass concentrations.

Figure 3 shows that air masses on the Antarctic continent were transported over the Antarctic plateau during the prior 5 days. Considering that coarse particles can be removed efficiently from the atmosphere through dry deposition during transport, isolation from coastal regions might account for gradient features of aerosol number concentrations in coarse mode. In other words, coarse particles are supplied only slightly from coastal regions into the Antarctic plateau during summer. The aerosol number concentrations increased markedly in all size ranges (D_p >0.3 μm) under strong wind conditions. Therefore, the wind-blowing release of aerosol particles might play an important role in maintaining the aerosol system over the continent in addition to gas-to-particle conversion.

3-3 Morphology of aerosol particles collected during the JASE traverse

Figure 6 depicts examples of SEM images of aerosol particles collected during the JASE traverse. Figure 6a shows that most aerosol particles in fine mode had a satellite structure. The satellite particles were dominant in all samples in fine mode (D_p: 0.2–2 μm). The satellite particles were often observed also in coarse mode ($D_p > 2$ μm) in this study. Yamato et al. (1987) used chemical tests (Ca thin film method) to show that satellite particles consisted of H_2SO_4 in the Antarctic troposphere during summer. Figure 6b shows that aerosol particles without a satellite structure were also observed in coarse mode. Most non-satellite particles in coarse mode had a solid core with irregular shape and crystal-like shape. In addition, stain around the solid core was identified often in coarse mode, as depicted in Fig. 6b. Some coarse particles were satellite particles with irregular solid cores (not shown). Presence of the stain and satellite structure in coarse and fine modes suggests strongly that these particles had liquid phase in the atmosphere.

3-4 Aerosol constituents and mixing states during the JASE traverse

Figure 7 presents examples of EDX spectra of each aerosol particle collected during the JASE traverse. Although strong peaks of C, O, and Ni were detected in all samples, these peaks were derived from the sample substrate. Therefore, C, O, and Ni were excluded from discussion in this study. As portrayed in Fig. 7a, strong peaks of S were observed from aerosol particles with a satellite structure. Comparison among the elemental compositions, morphology (satellite structure), and previous investigations by Yamato et al. (1987) and Hara et al. (2013) showed that these particles might consist mainly of H_2SO_4 and CH_3SO_3H, which are derived mainly from oceanic bio-activity. Because EDX can provide only elemental information, we cannot distinguish SO_4^{2-} from $CH_3SO_3^-$. Hereinafter, we designate these aerosol particles as “sulfate particles”.

In fact, S and K were detected from aerosol particles as shown in Fig. 7b. Aerosol particles containing S and K had no satellite structure. Similar aerosol particles were identified in aerosol samples taken in the lower free troposphere – upper free troposphere in Antarctic region (Hara et al., 2010, 2013).

Peaks of Mg and S were obtained from aerosol particles as portrayed in Fig. 7c. Atomic ratios of Mg and S of the aerosol particles containing only Mg and S were compatible with the ratios of $MgSO_4$. Mg-rich sulfate particles in the lower troposphere over Syowa Station were identified dominantly in air masses transported from the Antarctic continent (Hara et al., 2013). Hara et al. (2013) reported that Mg-rich sulfate particles in the Antarctic atmosphere were associated with sea-salt fractionation and sea-salt modification. Details of Mg-rich sulfate particles and sea-salt fractionation are discussed in section 3-7.

Aerosol particles containing Ca and S were also observed in this study (Fig. 7d). Because of the atomic ratios of Ca and S, particles of this type might be $CaSO_4$ particles. $CaSO_4$ particles were identified in the lower troposphere on the Antarctic region (Hara et al., 2010, 2013). Actually, $CaSO_4$ is well known as a major mineral constituent (gypsum). Moreover, Marion and Farren (1999) and Geilfus et al. (2013) pointed out $CaSO_4$ (gypsum) formation by sea-salt fractionation on sea ice in polar regions. However, the origins of $CaSO_4$ particles in the Antarctic atmosphere remain unclear.

Peaks of Na, Mg, S, and Cl were obtained in aerosol particles as shown in Fig. 7e. These elements are major seawater constituents. When artificial NaCl particles were analyzed using SEM-EDX, the peak height of Cl was slightly higher than that of Na.

Consequently, the particle in Fig. 7e might be identified as partly Cl-depleted sea-salt particles. In addition, Na, Mg, and S were detected from the aerosol particle in Fig. 7f. Compared to the aerosol particle in Fig. 7e, the peak height of S relative to Na was higher in the particle in Fig. 7f. Additionally, the height of Mg relative to Na was higher than that of sea-salt particles depicted in Fig. 7d. The particle in Fig. 7f might be identified as a wholly Cl-depleted sea-salt particle with slight Mg-enrichment. Although Na, Mg, and S were detected from the aerosol particle in Fig. 7g, the peak height of S was lower than the particles in Figs. 7e-7f. In addition, the particle in Fig. 7g might be identified as a wholly Cl-depleted sea-salt particle. Hereinafter, we designate wholly Cl-depleted particles as “modified sea-salt particles”. Less Cl-depleted sea-salt particles and partially Cl-depleted sea-salt particles were divided into “sea-salt particles” in this study. Modification of sea-salt particles is discussed in section 3-6. Although Mg is a major sea-salt constituent, Mg was not detected from aerosol particles containing Na, K, and Cl, as portrayed in Fig. 7h. A particularly strong K peak relative to Na peak was identified clearly from the particle in Fig. 7h. Na is a dominant constituent in sea-salt particles. Therefore, particles of this type were identified as “sea-salt-like particles” in this study. The sea-salt-like particles were observed only at sampling sites on the way from Dome F to the meeting point in the incoming traverse on 21–23 December, 2007 when aerosol particles were collected under conditions with drifting snow.

In fact, Si, Al, and S were detected from solid particles as shown in Fig. 7i. Results show that Al and Si were major constituents. Therefore, particles of this type might be identified as mineral particles. Here, aerosol particles containing Si and Al were classified into “mineral particles”. Furthermore, stain and satellite structures were observed around irregular solid core in some mineral particles. Considering that S was detected in mineral particles (irregular solid particles) satellite structure, these particles were likely to be mineral particle coated by acidic sulfates and H_2SO_4. In addition, internal mixtures of minerals and sea-salt particles were often identified in this study

(Fig. 7j).

3-5 Horizontal distributions of aerosol constituents during the JASE traverse

To compare quantitatively horizontal distributions of each aerosol constituent and mixing states, we estimated the relative abundance (number fraction) of each type of aerosol constituent. Considering the mean analyzed particles in each sample in this study, the detection limit of relative abundance was ca. 0.1% in fine mode and 1-2% in coarse mode except for samples with lower aerosol density on the substrate in coarse mode. Figures 8 and 9 show horizontal distributions of relative abundance of aerosol mixing states in coarse and fine modes during the incoming traverse (14 November – 27 December 2007) and the outgoing traverse (27 December 2007 – 24 January 2008).

3-5-1 Sea-salts

In coarse mode, major aerosol particles were sea-salt particles, modified sea-salt particles and sulfate particles. The relative abundance of sea-salt particles in coarse mode was larger than 40% near the coast in the incoming traverse. Relative abundance of sea-salt particles in coarse mode decreased gradually in inland areas, with exception of the high abundance at sampling sites in 77–76 °S on the way from Dome F Station to the meeting point in the incoming traverse (Fig.8d). As described above, sea-salt-like particles (Na–K–Cl) were observed predominantly in coarse mode at these sites. With the gradual decrease of the relative abundance of sea-salt particles, the relative abundance of the modified sea-salt particles increased gradually up to 40% on the Antarctic plateau. By contrast, the modified sea-salt particles were dominant in fine mode in the incoming traverse. Because of the predominance of sulfate particles in fine mode, the relative abundance of sea-salt particles and the modified sea-salt particles was less than 6.8% even at latitudes lower than 72 °S and less than 2.8% at latitudes higher than 72 °S during the incoming traverse. According to the 5-day backward trajectory as depicted in Fig. 3, transport from the coasts was found only at 69–71 °S during the incoming traverse, whereas air masses in the inland area (>72 °S) were transported over the continent during the prior 5 days. Therefore, isolation from the coastal regions might cause gradual distributions of sea-salt particles and modified sea-salt particles in the continent. The transport pathway, however, cannot account for the high relative abundance of sea-salt particles and the modified sea-salt particles, for example at 72‑73 °S and at 77–76 °S. As depicted in Fig. 4, the aerosol number concentrations increased considerably, particularly in coarse mode, under strong wind conditions in the incoming traverse to the meeting point. Consequently, high aerosol number concentrations and their high relative abundance might result from redistribution of aerosol particles such as sea-salt particles from the snow surface. Therefore, the horizontal distribution of relative abundance of sea-salt particles and the modified sea-salt particles on the

Antarctic continent during summer might be associated with the transport pathway and release from the snow surface via wind-blowing.

Relative abundance of sea-salt particles and the modified sea-salt particles in coarse mode ranged mostly lower than 60% during the outgoing traverse. Although the total relative abundance of sea-salt particles and the modified sea-salt particles in coarse mode was similar to that in the incoming traverse except for the high relative abundance under strong wind conditions, the modified sea-salt particles were dominant in the outgoing traverse. However, the relative abundance of sea-salt particles and the modified sea-salt particles in fine mode was mostly less than 0.5% in inland areas during the outgoing traverse. In some samples taken on the Antarctic plateau, sea-salt particles and the modified sea-salt particles were not detected in fine mode. Compared to the horizontal distributions of sea-salt particles and the modified sea-salt particles in fine mode during the incoming traverse, relative abundances of sea-salt particles and the modified sea-salt particles were remarkably lower. Mass concentrations of sea-salts (Na^+) in aerosol particles show a minimum at Syowa and Dome F stations during summer (Hara et al., 2004). In addition, the relative abundance of sea-salt particles and the modified sea-salt particles decreased considerably over Syowa Station (Hara et al., 2013). Although blizzard attributable to approaching cyclone occurs until early December at Syowa Station, few blizzards occur usually in mid-December – January

(Sato and Hirasawa, 2007). The seasonal feature of approaching cyclone are closely related to the origins of air masses over the Antarctic continent, as suggested by Suzuki et al. (2013). Therefore, the difference of the relative abundance between in the incoming traverse and in the outgoing traverse might correspond to seasonal features of sea-salt particles, air mass origins, and transport pathway from the end of spring to summer on the Antarctic continent.

3-5-2 Sulfates

As classified in section 3-4, the following aerosol particles containing sulfates were identified in this study: (1) sulfate particles, (2) modified sea-salt particles, (3) sulfate particles containing K, (4) $MgSO_4$ particles, (5) $CaSO_4$ particles, and (6) mineral particles internally mixed with sulfates. Because horizontal distributions of the modified sea-salt particles and mineral particles internally mixed with sulfates were described, respectively, in sections 3-5-1 and 3-5-3, their description is excluded from this section.

Figures 8 and 9 show that sulfate particles were the major aerosol particles in coarse mode and that they were dominant in fine modes. Particularly, the mean relative abundance of sulfate particles in fine mode was 98.5% in the incoming traverse and 99.5% in the outgoing traverse. In some samples taken on the Antarctic plateau, the relative abundance of sulfate particles in fine mode reached 100% in incoming and outgoing traverses. Considering detection limits of the relative abundance in fine mode, the upper limit of relative abundance of aerosol particles other than sulfate particles might be less than 0.1% in these samples (100% abundance of sulfate particles). Higher relative abundance of sulfate particles in the outgoing traverse is likely to result from (1) increase of the number concentrations of sulfate particles in fine mode by particle growth of ultrafine sulfate particles by hygroscopicity, (2) cloud processes, and (3) decrease of the number concentration of sea-salt particles and the modified sea-salt particles during the summer. Indeed, mass concentrations of nss-SO_4^{2-} and sea-salts (Na^+), respectively showed a maximum and minimum in the summer (January–February) along the Antarctic coast and inland (e.g., Minikin et al., 1998; Hara et al., 2004; Weller and Wagenbach, 2007; Preunkert et al., 2008; Udisti et al., 2012). The relative abundance of sulfate particles in fine mode was 82.9–98.2% (mean, 93.1%) in the boundary layer and 96.2–99.7% (mean, 98.1%) in the lower free troposphere over Syowa Station, Antarctica during mid-November through January (Hara et al., 2013). Consequently, the relative abundance of sulfate particles in fine mode near the surface on the Antarctic continent was similar to that in the lower free troposphere over the Antarctic coast (Syowa Station). The relative abundance of sulfate particles in coarse mode often exceeded 40% on the Antarctic continent during the JASE traverse. Such a high relative abundance of coarse sulfate particles was not observed in the boundary layer but often in the lower free troposphere over Syowa Station (Hara et al., 2013). As described above, “sulfate particles” in this study did not contain Na, Al, and Si. Therefore, these particles might be composed of SO_4^{2-} and $CH_3SO_3^-$ as suggested by Hara et al. (2005). In addition, chemical tests using Ca thin film method implied that aerosol particles containing SO_4^{2-} were present as acidic states (i.e., sulfuric acid particles) (Yamato et al., 1987a, 1987b). Consequently, sulfate particles might be grown to coarse mode through (1) hygroscopic growth, (2) cloud processes, (3) heterogeneous sulfate formation and (4) coagulation and condensation of condensable vapors (e.g., H_2SO_4 gas) under conditions with low number concentrations of pre-existing particles on the Antarctic continent.

The relative abundance of K-rich sulfate particles ranged from not detected (n.d.) to 2.0% in coarse mode and ranged from n.d. to 0.9% in fine mode in this study. Although K-rich sulfate particles were obtained in a few samples in coarse mode, these particles were observed often in fine mode in this study. Moreover, K-rich sulfate particles were often observed in the incoming traverse. In addition, the relative abundance of K-rich sulfate particles in the incoming traverse was higher than that in the outgoing traverse. K-rich sulfate particles were distributed also in boundary layer – upper free troposphere over Syowa Station (Hara et al., 2010, 2013). Actually, K-rich sulfate particles cannot be formed through gas-to-particle conversion from aerosol precursors derived from oceanic bioactivity. Therefore, K-rich sulfate particles might be non-biogenic aerosol particles. As discussed by Okada et al. (2001, 2008) and Niemi et al. (2005), K-rich sulfate particles and nss-K in aerosol particles are released from combustion processes such as biomass burning.

As discussed above and by Hara et al. (2013), K-rich sulfate particles might have originated from biomass burning and fossil fuel combustion. As shown in Figure 3, direct transport from outsides of the Antarctic Circle was not found for the prior 5 days. Moreover, the source strength of combustion of fossil fuel is extremely low in Antarctic regions. Particularly, biomass burning does not occur in the Antarctic regions. Therefore, sulfate particles containing K were likely to have been transported to the Antarctic continent via the free troposphere during summer for the prior 5 days. The presence of combustion-origin aerosol particles (e.g., sulfate particles containing K) was supported by high BC concentrations at the South Pole in the summer (Bodhaine, 1995). This difference of relative abundance in incoming and outgoing traverses might be attributed to seasonal features of K-rich sulfate particles, air mass origins, and transport pathway in the inland area during late spring – summer.

The relative abundance of Mg-rich sulfate particles (probably $MgSO_4$) examined in this study ranged from n.d. to 1.8% in coarse mode and ranged from n.d. to 0.5% in fine mode. During the incoming traverse, Mg-rich sulfate particles were found frequently in fine mode at sampling sites in 69.2–72.5 °S, although those were observed in some aerosol samples collected at plateau sites. However, Mg-rich sulfate particles were identified mainly on the Antarctic plateau during the outgoing traverse. The relative abundance of Mg-rich sulfate particles was lower in the outgoing traverse than that in the incoming traverse. Mg-rich sulfate particles were distributed mostly in fine mode over Syowa Station (Hara et al., 2013). An earlier investigation (Hara et al., 2013) showed that Mg-rich sulfate particles were associated with sea-salt fractionation (Mg separation) and modification (Cl loss by heterogeneous reactions). Consequently, the presence of Mg-rich sulfate particles in the atmosphere near the surface on the Antarctic continent in this study strongly suggests that sea-salt fractionation occurs on the Antarctic continent during summer. Details of sea-salt fractionation are discussed in section 3-7.

Relative abundance of Ca-rich sulfate particles (probably $CaSO_4$) ranged from n.d. to 8.7% in coarse mode and ranged from n.d. to 0.2% in fine mode in the incoming traverse. However, the relative abundance of Ca-rich sulfate particles in the outgoing traverse was n.d. in coarse mode and ranged from n.d. to 0.1% in fine mode. Although Ca-rich sulfate particles were not detected in most samples in either traverses, Ca-rich sulfate particles were identified mainly near coasts (<72°S). Although Ca-rich sulfates such as gypsum are mineral components, most Ca-rich sulfates were not mixed with Al and Si, which are major elements of mineral particles. Consequently, horizontal distributions and external mixing states of Ca-rich sulfates imply the important contribution of non-mineral origins such as sea-salt fractionation on sea ice as reported by Geilfus et al. (2013).

3-5-3 Minerals

The relative abundance of mineral particles ranged in n.d. – 14.6% in coarse mode and n.d. – 0.4% in fine mode during the incoming traverse, although the relative abundance ranged in n.d. – 5.7% in coarse mode and n.d. – 0.1% in fine mode during the outgoing traverse. Mean relative abundance in coarse mode was 3.8 and 1.8 % in incoming and outgoing traverses, respectively, and that in fine mode was 0.1 % and 0.01 % in incoming and outgoing traverses. Most mineral particles were internally mixed with sea-salts or sulfates in this study. Although the mineral particles were observed mainly in coarse mode, SEM-EDX analysis showed that the size of irregular solid cores containing Al and Si was of sub-micrometer in this study. The size of irregular solid cores was coincident with the size distribution of water-insoluble particles (mainly mineral particles) in ice cores taken in Antarctica (e.g., Ram and Gayley, 1988; Delmonte et al., 2004, 2007). In contrast, external mixing states of mineral particles were often present in the boundary layer and free troposphere over Syowa Station located at the coast (Hara et al., 2006, 2013). The difference of mixing states of mineral particles suggests that mixing states of mineral particles changed gradually to internal mixtures through coagulation in cloud processes, and through heterogeneous reactions during their transport to inland areas. As described above, a change of mixing state of mineral particles can engender particle sizes greater than the external mixing states of mineral particles. Because of the higher dry deposition velocity of coarse aerosol particles, internal mixing among minerals, sulfate, and sea-salts during transport might enhance the efficient deposition of minerals onto the snow surface on the Antarctic continent.

3-6 Sea-salt modification during the JASE traverse

3-6-1. Sea-salt modification in coarse and fine modes

Figure 10 portrays examples of ternary plots (Na–S–Cl) of sea-salt particles and the modified sea-salt particles during the JASE traverse. To avoid misunderstanding of sea-salt modification, the internal mixed sea-salt and mineral particles were excluded from the ternary plots and discussion. Red and blue stars respectively denote atomic ratios of bulk seawater ratios and wholly Cl depleted sea-salt particles by SO_4^{2-}. The black line represents the stoichiometric line from the sea salt particles with bulk seawater ratio (red star) to the Cl-depleted sea salt particles by sulfates (blue star). When Cl in sea-salt particles is replaced stoichiometrically to SO_4^{2-} by heterogeneous reactions, each sea salt particle is distributed along the stoichiometric line.

Most sea-salt particles in coarse mode had Cl ratios lower than the seawater ratio in this study. Although S ratios increased gradually with decreased Cl ratios in sea-salt particles, the S ratios in sea-salt particles were less than those of the stoichiometric line on the Antarctic continent during summer, which suggests that sea-salt particles were modified not only with SO_4^{2-} but also with acidic species other than acidic sulfur species such as SO_4^{2-}. Plausible acidic species other than SO_4^{2-} and $CH_3SO_3^-$ for Cl loss from sea-salt particles are reactive nitrogen oxides such as HNO_3, N_2O_5, and NO_3 (e.g.., Hara et al., 1999) and organic acids (Kerminen et al., 2000; Laskin et al., 2012). Previous studies of aerosol chemistry in Antarctic regions showed that NO_3^- concentrations were higher than those of organic acids (oxalate, formate, and acetate) (Jourdain and Legrand, 2002; Weller et al., 2002, 2007; Rankin and Wolff, 2003; Legrand et al., 2004; Hara et al., 2010; Weller et al., 2011). Furthermore, higher concentrations of reactive nitrogen oxides (e.g., HNO_3 and NO) were observed on the Antarctic continent and coasts during summer (Davis et al., 2004; Dibb et al., 2004; Jones et al., 2011). Details of origins of the reactive nitrogen oxides are discussed in the next section. Therefore, heterogeneous NO_3^- formation on sea-salt particles might make an important contribution to sea-salt modification in inland areas during summer. In contrast to sea-salt modification in coarse mode, most of the modified sea-salt particles in fine mode were distributed in the Cl ratio of ca. 0% and higher S atomic ratio relative to the modified sea-salt particles. Therefore, fine sea-salt particles on the Antarctic continent might be modified preferentially with acidic sulfur species such as SO_4^{2-} and $CH_3SO_3^-$.

3-6-2. Horizontal features of sea-salt modification on the Antarctic continent

Figures 11 and 12 respectively portray horizontal features of the atomic ratios of Cl/Na and S/Na of sea-salt particles and the modified sea-salt particles in coarse and fine modes during the incoming and outgoing traverses. The internal mixing particles between sea-salts and minerals were excluded from the box plots. A latitudinal gradient of Cl/Na ratios in coarse mode was observed in 69–71 °S in the incoming traverse. High Cl depletion was identified in most aerosol samples obtained for the Antarctic plateau, except for some samples taken at 76.5-76 °S in the incoming traverse from Dome F to the meeting point. In spite of the latitudinal gradient of Cl/Na ratios in coarse mode in 69–71 °S in the incoming traverse, the S/Na ratio increased slightly. Similarly, median S/Na ratios of sea-salt particles and the modified sea-salt particles in coarse mode were distributed approximately around 0.2 during the JASE traverse. When sea-salt particles are modified solely with SO_4^{2-}, the S/Na ratios in sea-salt particles are 0.5. As suggested in ternary plots in Fig. 10, therefore, NO_3^- contributed dominantly to sea-salt modification in coarse mode on the Antarctic continent.

Hara et al. (2005, 2013) reported that most sea-salt particles in coarse mode were modified slightly over Syowa station in the summer. Some were modified with SO_4^{2-}. Consequently, the acids contributing to sea-salt modification differed between those in coarse sea-salt particles on the Antarctic coasts and those on the continent during summer. The air mass history and origins of coarse sea-salt particles, NO_3^-, and its precursors on the Antarctic continent must be discussed to elucidate the strong contribution of NO_3^- to sea-salt modification. The 5-day backward trajectory, as depicted in Fig. 3, shows that continental air masses on the Antarctic plateau had not been transported directly from coasts during the prior 5 days. Because of efficient dry deposition of coarse aerosol particles, coarse particles suspended at the Antarctic coasts might be transported only slightly to the Antarctic continent (particularly the Antarctic plateau) for longer than 5 days. As discussed in sections of 3-2 and 3-5-1, most coarse sea-salt particles on the Antarctic plateau were likely to have originated from surface snow on the Antarctic continent. Figures 11 and 12 show that high Cl/Na ratios on the Antarctic plateau often corresponded to conditions with strong winds and drifting snow. Consequently, sea-salt particles might have high Cl/Na ratios immediately after release from the snow surface. Then, sea-salt particles in coarse mode might be modified gradually with reactive nitrogen oxides such as HNO_3 in the continental atmosphere during transport over the Antarctic continent.

Field measurements of the surface snow in polar regions (e.g., Davis et al., 2001, 2004; Frey et al., 2009; Jones et al., 2011) implied photochemical-recycling mechanisms of snow-nitrate near the surface of polar regions during summer. Indeed, high NO concentrations (order of several hundred pptv) were observed at the South Pole Station during summer (Davis et al., 2001; Neff et al., 2008). Actually, NO_x can be converted to HNO_3 in the atmosphere. Therefore, the high NO_x concentration during summer on the Antarctic plateau might engender efficient HNO_3 production near the surface, as suggested by Dibb et al. (2004). Considering the high NO_3^- concentration in the surface snow around Queen Maud Land, especially around Dome F Station (Bertler et al., 2005), considerable HNO_3 production in the atmosphere might occur on the Antarctic plateau. Therefore, sea-salt modification in coarse mode through heterogeneous reactions with reactive nitrogen oxides (mainly HNO_3) might occur preferentially on the Antarctic continent during summer.

By contrast, S/Na ratios in fine sea-salt particles exceeded mostly 0.5 during the traverse. The high S/Na ratios in each sea-salt particle in fine mode imply that sulfates were formed on the fine sea-salt particles through heterogeneous reactions with gaseous sulfur species such as H_2SO_4 and SO_2. High S/Na ratios in the modified sea-salt particles were also obtained in the boundary layer and lower free troposphere over

Syowa Station during summer (Hara et al., 2013). Because of the longer residence time of fine aerosol particles, the modified sea-salt particles in fine mode with high S/Na ratio might be supplied by transport from coastal regions to the continent and might be formed through heterogeneous processes during transport.

3-7 Sea-salt fractionations on the Antarctic continent during summer

3-7-1. Sea-salt fractionations in coarse and fine mode

Figure 13 shows examples of ternary plots of sea-salts (Na, Mg, and S) and Mg-rich sulfates in coarse and fine modes. Internal mixtures of sea salts and minerals were removed from the ternary plots. In the ternary plots, sea-salt particles with bulk seawater ratio are distributed around the red star (bulk seawater ratio). When the sea-salt particles are modified by sulfate and are not fractionated, they are distributed around the stoichiometric line between the red star (seawater ratio) and the blue star (modified sea-salt ratio with sulfate). With sea-salt fractionation by precipitation of Na-salts such as mirabilite (Na_2SO_4 $10H_2O$) and hydrohalite ($NaCl$ $2H_2O$) (Hara et al., 2012), Mg in sea-salt particles can be enriched gradually. For cases in which sea-salt fractionation (replacement between Na and Mg) occurs without sea-salt modification by sulfate, sea-salt particles are distributed around the stoichiometric line between the red star (bulk seawater ratio) and the cyan star ($MgCl_2$). When sea-salt fractionation and sea-salt modification by sulfate occur stoichiometrically and simultaneously, sea-salt particles are distributed around the stoichiometric line between the red star (seawater ratio) and the green star ($MgSO_4$).

Because sea-salt particles were modified dominantly during JARE (as shown in Figs. 10-12), most sea-salt particles and the modified sea-salt particles in coarse mode were distributed in 60–90% of the Na atomic ratio. The Mg ratios in coarse mode, however, were greater than the stoichiometric line of sea-salt modification (between the red star and blue star). Some of the modified sea-salt particles had Mg ratio ≈ 0, even in coarse mode. The Mg ratios in fine mode were distributed at Mg ratio ≈ 0 and around the stoichiometric line between the red star (seawater) and green star ($MgSO_4$). Here, we designate sea-salt particles with Mg ratio ≈ 0 as “Mg-free sea-salt particles”. In addition to Mg-free sea-salts, $MgSO_4$ particles were often observed in this study, as shown in Figs. 7-9 and 13. Similar distributions were observed in sea-salt particles and the modified sea-salt particles collected over Syowa Station (Hara et al., 2013). The Mg/Na ratios cannot be changed by sea-salt modification. Sea-salt fractionation in sea ice regions during winter through spring (e.g., precipitation of mirabilite and hydrohalite) can promote Mg enrichment in sea-salt particles, as reported by Hara et al. (2012). Consequently, sea-salt fractionation in sea ice regions cannot account for the presence of Mg-Free sea-salt particles during spring–summer. Because Mg-rich sulfate particles over Syowa Station were identified in the air masses from the Antarctic continent (Hara et al., 2013), discussion must address horizontal features of Mg-rich sulfates, Mg-rich sea-salt particles and Mg-free sea-salt particles on the Antarctic regions. Then it will be possible to assess the possibility of sea-salt fractionation on the Antarctic continent.

3-7-2. Horizontal features of sea-salt fractionation on the Antarctic continent

To elucidate sea-salt fractionation on the Antarctic continent during summer, we must compare horizontal features of sea-salt constituents on the Antarctic continent. Figures 14 depicts horizontal features of Mg/Na ratios in coarse and fine modes during the JASE traverse. Internal mixtures of sea salts and minerals were removed from the plots. Mg/Na ratios in fine mode were varied largely in coming traverse. Because of lower relative abundance of sea-salt particles and the modified sea-salt particles in fine mode, horizontal features of Mg/Na ratios in fine mode were obtained only in 69–73.5 °S in the incoming traverse. The large variation of Mg/Na ratios might be attributed to presence of Mg-rich sea-salt particles and Mg-free sea-salt particles in fine mode, as shown in the ternary plots (Fig. 13). Median Mg/Na ratios in coarse mode were approximately 0.32 in the incoming traverse and 0.31 in the outgoing traverse. Because of Mg/Na ratio ≈ 0.11 in bulk seawater (e.g., Wilson, 1975), Mg might be enriched in most sea-salt particles in coarse mode. In addition, Mg-free sea-salt particles (Mg/Na ratio ≈ 0) in coarse mode were identified often on the Antarctic continent, particularly on the Antarctic plateau. For example, Mg-free sea-salt particles in coarse mode were dominant in three samples taken on 21–23 December, 2007 (76.6–76.0 °S) in the traverse from Dome F to the meeting point, as shown in Fig. 14. The presence of Mg-free sea-salt particles in coarse mode corresponded often to occurrence of drifting snow and high aerosol number concentrations in coarse mode in the incoming traverse. Mg-rich sea-salt particles, Mg-free sea-salt particles, and $MgSO_4$ particles were present also in fine mode on the Antarctic continent, although the low relative abundance of sea-salt particles and the modified sea-salt particles prevented us from elucidating the horizontal features of Mg/Na ratios on the Antarctic plateau. These horizontal features of Mg/Na ratios during the JASE traverse imply strongly that the fractionated sea-salt particles were distributed widely throughout the Antarctic continent during summer. Mg-free sea-salt particles were identified mainly in fine mode and rarely in coarse mode over Syowa Station (Hara et al., 2013). Figure 3 shows that air masses on the Antarctic plateau were isolated from coastal regions for the prior 5 days. The lower relative abundance of Mg-free sea-salt particles in coarse mode over Syowa Station suggests that Mg-free sea-salt particles and other fractionated sea-salt particles such as Mg-rich sulfates and Mg-rich sea-salts had not originated from coastal regions, considering the efficient dry deposition of aerosol particles in coarse mode. Aerosol particles on the Antarctic plateau, especially in coarse mode, were supplied to a marked degree from snow surface by wind blowing under strong conditions, as described above. Furthermore, Mg-rich sulfates and Mg-free NaCl were present in surface snow (Iizuka et al., 2012). Therefore, the fractionated sea-salt particles (Mg-rich sea-salt particles, Mg-free sea-salt particles, and $MgSO_4$ particles) might have originated from surface snow on the Antarctic continent. Considering that Mg-free sea-salt particles were often observed under strong wind conditions (especially on 21–23 December), strong winds might be necessary for the release of Mg-free sea-salt particles.

To explain the presence of Mg-rich sea-salt particles, Mg-free sea-salt particles and $MgSO_4$ particles on the snow surface of the Antarctic continent, it is necessary to discuss Mg separation processes. Redistribution of chemical constituents can occur through (1) seawater freezing (Marion and Farren, 1999; Hara et al., 2012), and (2) phase transformation by deliquescence and efflorescence (e.g., Ge et al., 1998; Wise et al., 2009, Woods et al., 2010). Sea-salt fractionation in seawater freezing depends on the temperature (Marion and Farren, 1999; Hara et al., 2012). The air temperature on the Antarctic plateau was often below -30 °C even during summer, as presented in Fig. 2 and previous investigations (King, Argentini and Anderson, 2006; Hirasawa et al., 2013). Air temperature might constitute an important condition for some sea-salt precipitation (e.g., ca. -34 °C and -36 °C for KCl and $MgCl_2$ 12 H_2O), as discussed by Marion and Farren (1999). Unlike sea-salts in seawater, however, sea-salts in snow on the Antarctic content were supplied solely by deposition of sea-salt particles that had been transported from coastal regions. When Mg separation is controlled only by lower temperatures, Mg-free sea-salt particles, Mg-rich sea-salt particles, and Mg-rich sulfate particles can be present in the Antarctic regions. However, Mg-free sea-salt particles were not observed over Syowa Station during winter in the air masses transported from the continent and coastal regions (Hara et al., 2013). This result implies that Mg separation was controlled not only by lower air temperature but also by other factors.

Figure 2 show that the air temperature near the surface had diurnal change also in continental areas. Furthermore, strong diurnal change of air temperatures and solar radiation engender water sublimation on the snow surface of the Antarctic continent (e.g., Kameda et al., 1997; Motoyama et al., 2005). With strong diurnal change of the air temperature, the relative humidity might exhibit a diurnal change near the snow surface on the Antarctic continent during summer. Actually, relative humidity reached ca. 100% during the local night time and reached a minimum in the afternoon at Kohnen Station during summer (Van As et al., 2005). The diurnal variation of the relative humidity can engender (1) phase transformation by deliquescence of available sea-salts on surface snow, (2) condensation and re-freezing of water vapor (e.g., formation of surface hoar) during local night time, and (3) enhancement of quasi-liquid layer and super-cold liquid on the surface snow. Laboratory experiments conducted for earlier studies (e.g., Ge et al., 1998; Wise et al., 2009, Woods et al., 2010) revealed that chemical constituents with lower deliquescence relative humidity (DRH) can be localized in the outer layer (surface) around a solid core through phase transformation by deliquescence. Although relative humidity was minimal in the afternoon at Kohnen Station (Van As et al., 2005), the minimum relative humidity (~89%) was often higher than the deliquescence relative humidity (DRH) of plausible sea-salts. Some examples are the following: NaCl, 75% (Tang and Munkelwitz, 1993); Na_2SO_4, 84% (Tang and Munkelwitz, 1994); $NaNO_3$, 75% (Tang and Munkelwitz, 1994); $MgCl_2$ $6H_2O$, 33% (Kelly and Wexler, 2005); $MgSO_4$, 42% (Wang et al., 2008); and KCl, 84% (Tang, 1980). Most plausible sea-salts can be wholly deliquescent even under minimum relative humidity (~89%) on the Antarctic continent. Therefore, phase transformation by deliquescence/efflorescence might not be key processes for Mg separation. With diurnal features of air temperature and relative humidity, re-condensation of water vapor on the snow surface during the local night time might induce enhancement of supercooled water in nanometer-to-micrometer scales, quasi-liquid layer, and re-freezing of water vapors and super-cold water such as hoar formation. Particularly, re-freezing processes on surface snow might cause sea-salt fractionation as well as seawater freezing. Therefore, we propose that the repetition of a diurnal cycle of relative humidity and water sublimation under colder conditions can engender Mg separation on the surface snow on the Antarctic continent during summer.

4 Concluding remarks

Measurements of aerosol size distribution and direct aerosol sampling were made in the Queen Maud Land, Antarctica during the JASE traverse from 14 November 2007 until 24 January 2008. The OPC measurements revealed that aerosol number concentrations decreased gradually with latitude under background conditions (without drifting snow or strong winds) on the Antarctic continent during summer. The estimated aerosol mass concentrations in the size range larger than 0.3 μm were 0.04–5.7 μg m^{-3}. When strong winds and drifting snow occurred, aerosol number concentrations increased precipitously, especially in coarse mode. Air masses were isolated from the Antarctic coasts during the prior 5 days. Therefore, coarse aerosol particles (mainly sea-salt particles) might be released from the snow surface by blowing winds.

Single-particle analysis using SEM-EDX revealed that major aerosol particles were sea-salt particles, modified sea-salt particles, and sulfate particles in coarse mode, and that the sulfate particles and modified sea-salt particles were dominant in fine mode during the JASE traverse. The K-rich sulfates, Mg-rich sulfates, Ca-rich sulfates, and minerals were minor aerosol constituents in coarse and fine modes. Although SO_4^{2-} and $CH_3SO_3^-$ contributed to sea-salt fractionation in coarse and fine modes over Syowa Station during summer (Hara et al., 2005, 2013), sea-salt particles were modified greatly with SO_4^{2-} and NO_3^- in coarse mode, and dominantly with SO_4^{2-} in fine mode in this study.

Precursors of particulate NO_3^- (e.g., HNO_3, and NO_x) might have originated from photochemical recycle of NO_3^- in surface snow and subsequent oxidation in the atmosphere. Median atomic ratios of Mg/Na in sea-salt particles and modified sea-salt particles in coarse and fine modes were often higher than the bulk seawater ratio. In addition, Mg-free sea-salt particles were identified on the Antarctic continent. Because the Mg/Na ratio cannot be changed by sea-salt modification, the presence of Mg-rich sea-salt particles, Mg-free sea-salt particles, and Mg-rich sulfate particles might be associated with sea-salt fractionation. Mg-free sea-salt particles in coarse mode were often identified under conditions with strong winds and drifting snow. Therefore, fractionated sea-salt particles were likely to have been released from the snow surface. This study proposed and assessed the hypothesis that sea-salt fractionation (Mg separation in sea-salts) occurs in surface snow on the Antarctic continent.

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Figure Captions

Figure 1 Traverse routes of Japanese team during JASE campaign. Black lines represent traverse routes between S16 and Dome F in incoming and outgoing traverse. The blue line represents traverse route from Dome F to meeting point in the incoming traverse. The red line represents traverse route from the meeting point to Dome F in outgoing traverse. The traverse route of the Swedish team was referred from Fujita et al. (2011).

Figure 2 Variations of latitudes, elevation, air temperature, and relative humidity during the JASE traverse. Cyan stars represent dates and locations of aerosol measurements and direct sampling.

Figure 3 5-day backward trajectories from every camp site in (a) incoming traverse from S16 to Dome F, and (b) traverse from Dome F (DF) to meeting point (MP), (c) traverse from meeting point to S16 in outgoing traverse. Black lines show the traverse route. Altitudes denote the height above the ground. Color code corresponds to the latitude at starting points of the trajectory.

Figure 4 Horizontal features of air temperature, elevation, wind speed, aerosol number concentrations and Junge slope during incoming traverse from S16 to the meeting point. Red boxes show conditions with drifting snow.

Figure 5 Horizontal features of air temperature, elevation, wind speed, aerosol number concentrations and Junge slope during outgoing traverse from the meeting point to S16. Red boxes show conditions with drifting snow.

Figure 6 SEM images of aerosol particles in (a) coarse mode and (b) fine mode.

Figure 7 EDX spectra of aerosol particles collected during the JASE traverse. Asterisks denote background peaks derived from the sample substrate.

Figure 8 Horizontal features of relative abundance of each aerosol constituent in (a–b) coarse and (c–d) fine modes during the incoming traverse.

Figure 9 Horizontal features of relative abundance of each aerosol constituent in (a–b) coarse and (c–d) fine modes during the outgoing traverse.

Figure 10 Ternary plots (Na–S–Cl) of sea-salt particles in coarse and fine modes during the JASE traverse. Red, and blue stars respectively denote atomic ratios of (1) bulk seawater, and (2) wholly Cl depleted sea-salt particles with sulfates. Black lines represent stoichiometric lines among constituents.

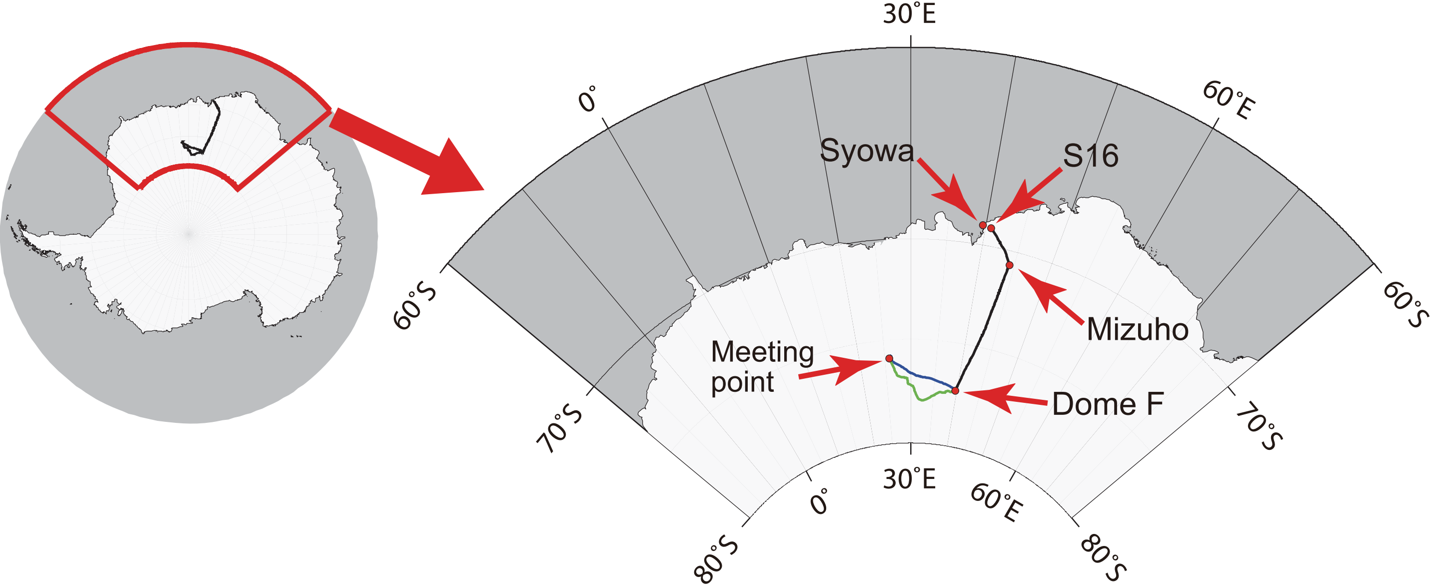
Figure 11 Horizontal features of atomic ratio of Cl/Na and S/Na in coarse and fine modes during the incoming traverse. In box plots, the top bar, top box line, black middle box line, bottom box line, and bottom bar respectively denote values of 90%, 75%, 50% (median), 25%, and 10%. The red line shows mean values.

Figure 12 Horizontal features of atomic ratio of Cl/Na and S/Na in coarse and fine modes during the outgoing traverse. In box plots, the top bar, top box line, black middle box line, bottom box line, and bottom bar respectively denote values of 90%, 75%, 50% (median), 25%, and 10%. The red line shows mean values.

Figure 13 Ternary plots (Na–Mg–S) of sea-salt particles in coarse and fine modes during the JASE traverse. Red, blue, cyan, and green stars respectively denote atomic ratios of (1) bulk seawater, (2) wholly Cl depleted sea-salt particles with sulfates, (3) $MgCl_2$, and (4) $MgSO_4$. Blue, pink, and red lines represent stoichiometric lines among constituents.

Figure 14 Horizontal features of the atomic ratio of Mg/Na in coarse and fine modes during the incoming traverse. In box plots, the top bar, top box line, black middle box line, bottom box line, and bottom bar respectively denote values of 90%, 75%, 50% (median), 25%, and 10%. The red line shows mean values.

Fig. 1


30˚E
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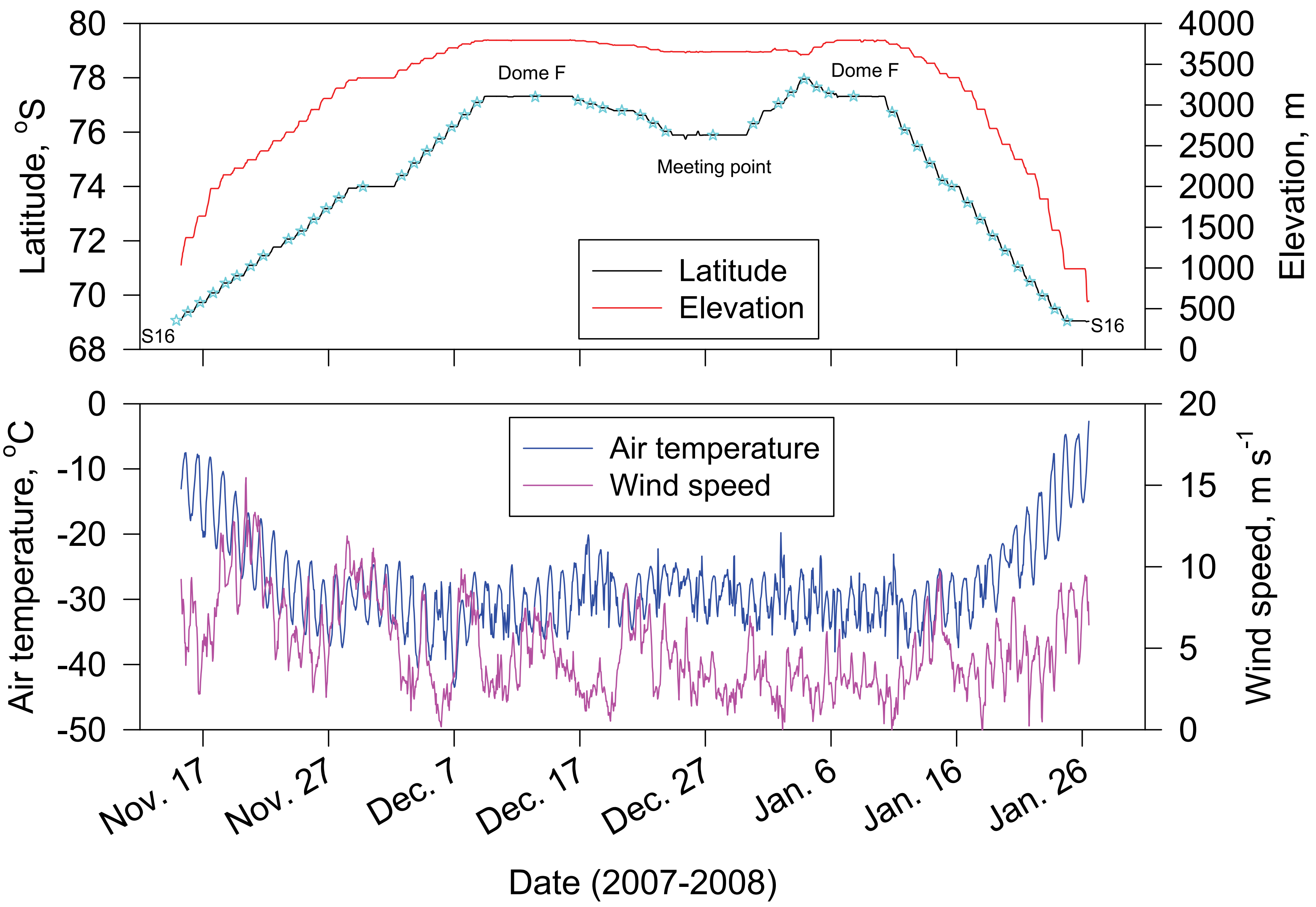
Latitude, ^oS
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68
4000
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Elevation, m
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Meeting point
S16
S16
Latitude
Elevation
Air temperature, ^oC
0
-10
-20
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-40
-50
20
15
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5
0
Wind speed, m s^{-1}
Air temperature
Wind speed
Nov. 17
Nov. 27
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Dec. 17
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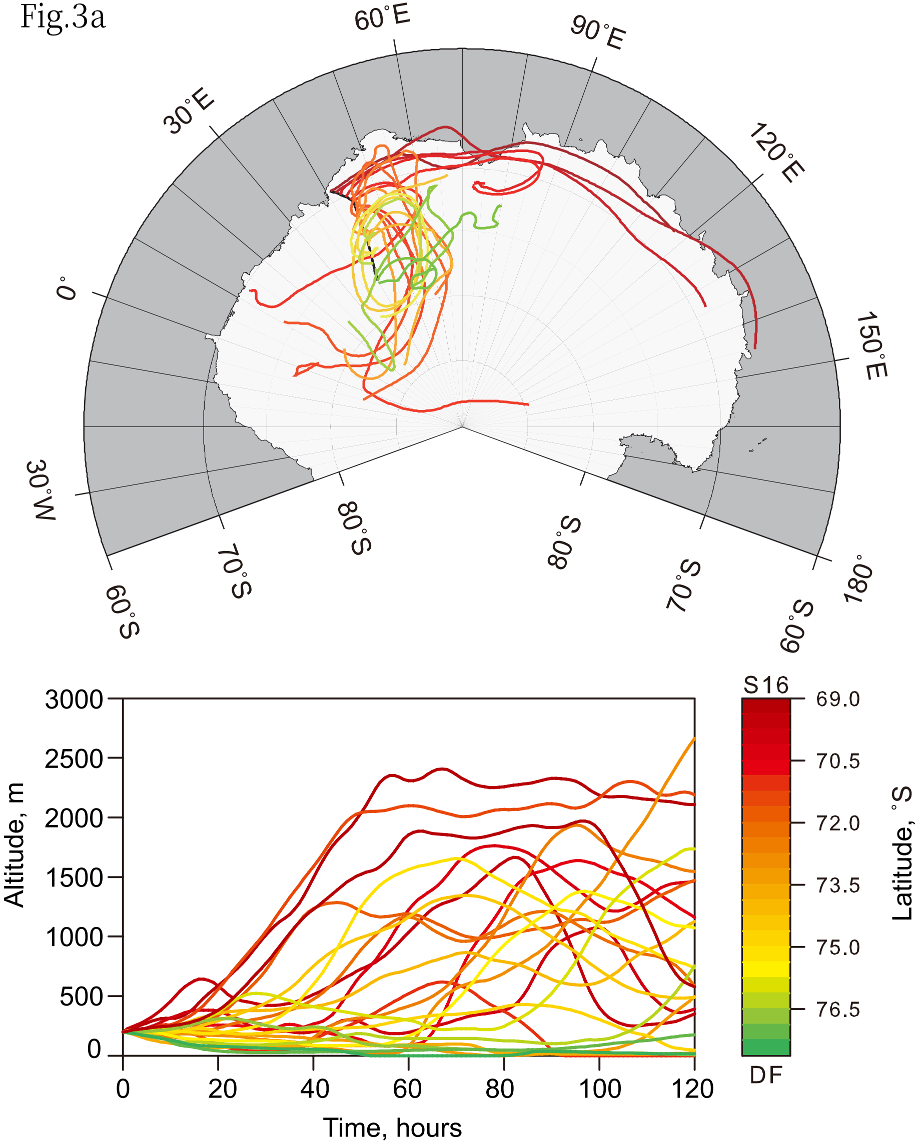
Date (2007-2008)

Fig. 2

Fig.3a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Latitude, °S

Fig.3b

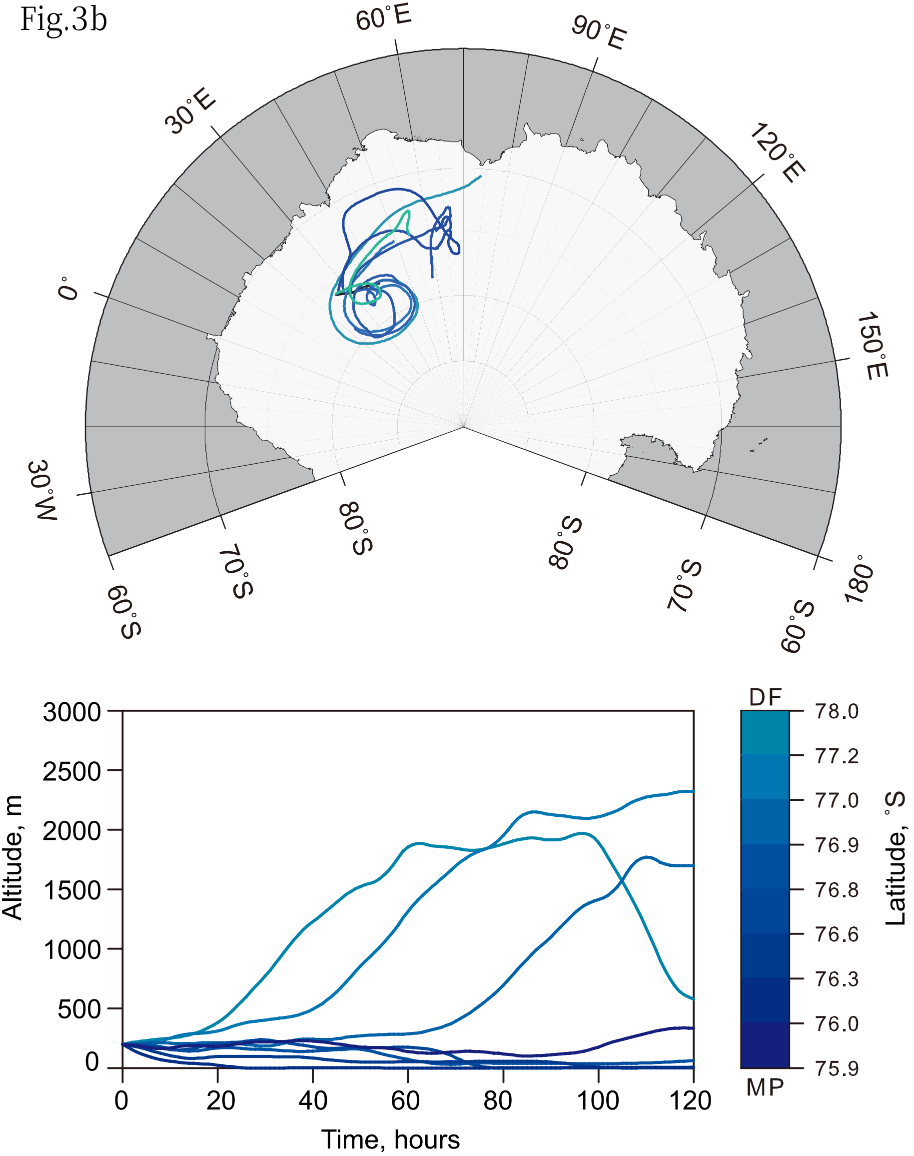
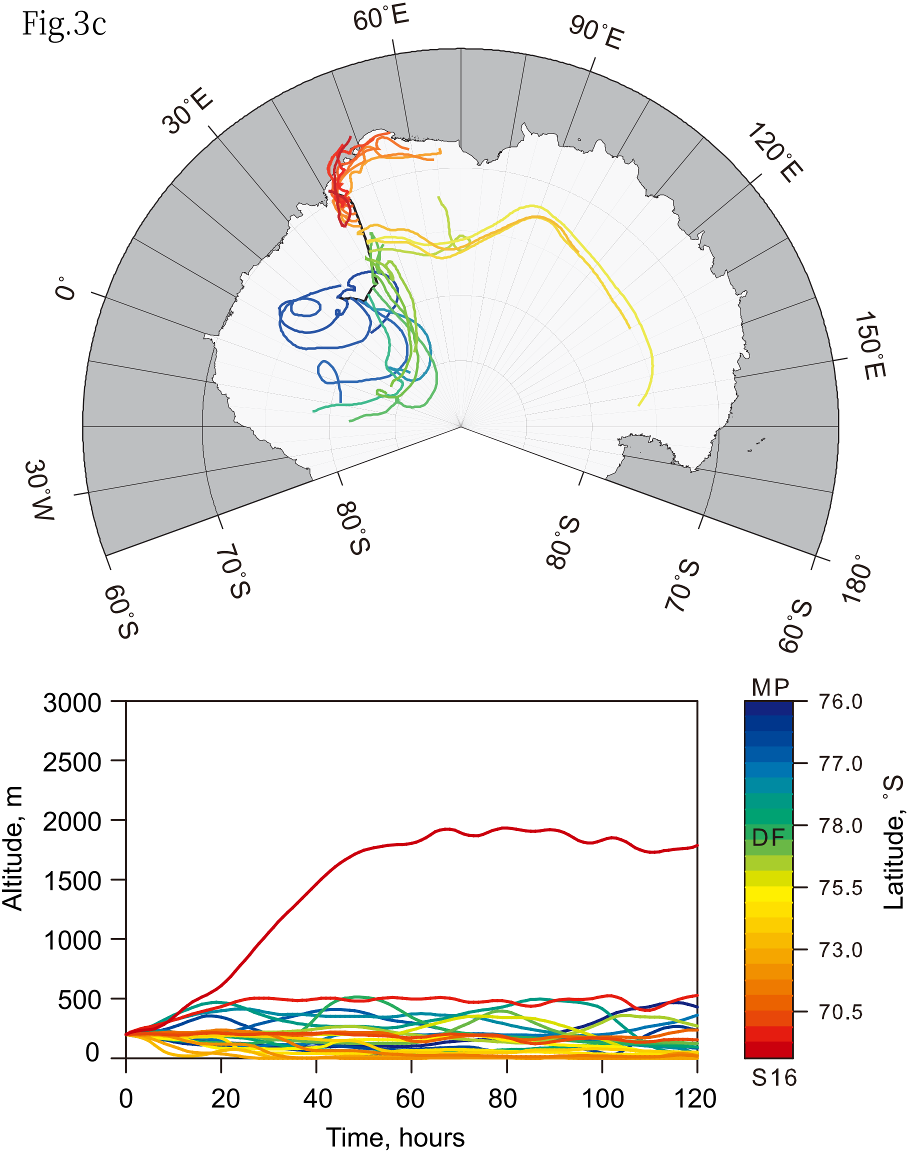

60°E
90°E
30°E
120°E
0°
150°E
30°W
180°
80°S
70°S
60°S
80°S
70°S
60°S
3000
2500
2000
1500
1000
500
0
Altitude, m
0
20
40
60
80
100
120
Time, hours
DF
MP
78.0
77.2
77.0
76.9
76.8
76.6
76.3
76.0
75.9
Latitude, °S

Fig.3c



60°E
90°E
30°E
120°E
0°
150°E
30°W
180°
80°S
70°S
60°S
80°S
70°S
60°S
3000
2500
2000
1500
1000
500
0
Altitude, m
0
20
40
60
80
100
120
Time, hours
MP
DF
S16
76.0
77.0
78.0
75.5
73.0
70.5
Latitude, °S

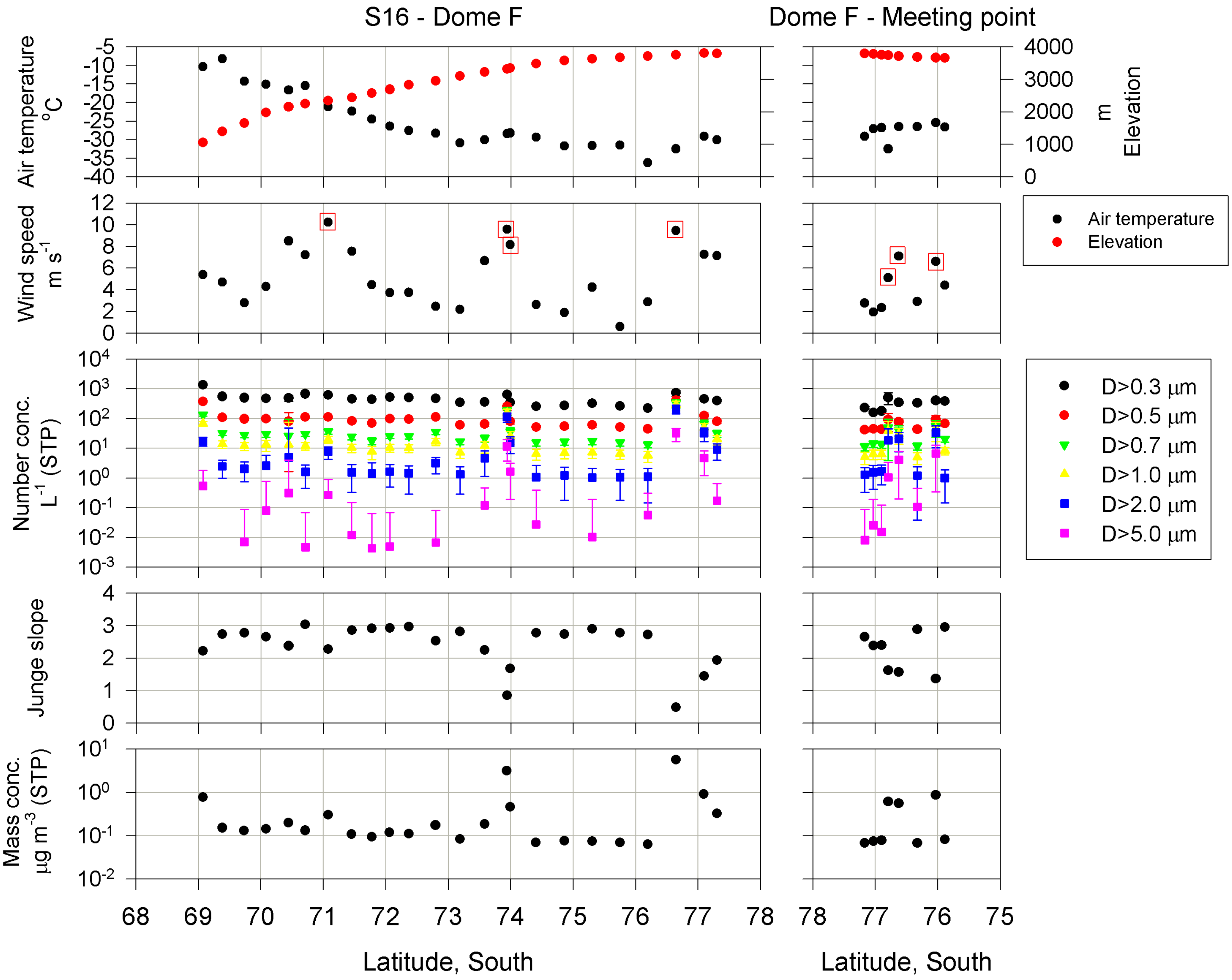

S16 - Dome F
Dome F - Meeting point
Air temperature
°C
-5
-10
-15
-20
-25
-30
-35
-40
4000
3000
2000
1000
0
m
Elevation
Wind speed
m s^{-1}
12
10
8
6
4
2
0
Air temperature
Elevation
Number conc.
L^{-1} (STP)
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
D>0.3 µm
D>0.5 µm
D>0.7 µm
D>1.0 µm
D>2.0 µm
D>5.0 µm
Junge slope
4
3
2
1
0
Mass conc.
µg m^{-3} (STP)
10^1
10^0
10^{-1}
10^{-2}
68
69
70
71
72
73
74
75
76
77
78
78
77
76
75
Latitude, South
Latitude, South

Fig. 4

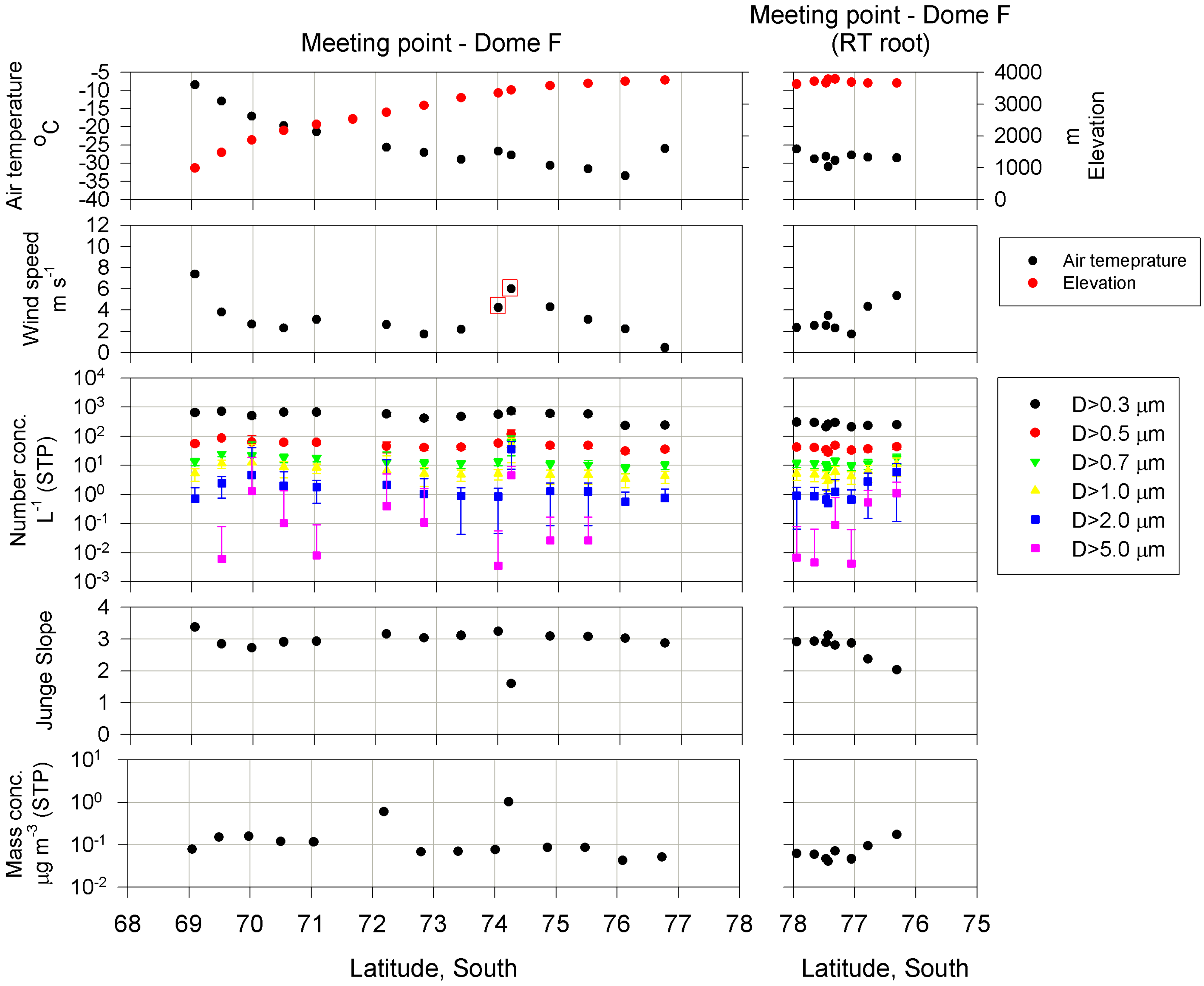

Meeting point - Dome F
Meeting point - Dome F
(RT root)
Air temperature
oC
-5
-10
-15
-20
-25
-30
-35
-40
4000
3000
2000
1000
0
m
Elevation
Wind speed
m s-1
12
10
8
6
4
2
0
Air temepraturе
Elevation
Number conc.
L-1 (STP)
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
D>0.3 µm
D>0.5 µm
D>0.7 µm
D>1.0 µm
D>2.0 µm
D>5.0 µm
Junge Slope
4
3
2
1
0
Mass conc.
µg m-3 (STP)
10^1
10^0
10^-1
10^-2
68
69
70
71
72
73
74
75
76
77
78
78
77
76
75
Latitude, South
Latitude, South

Fig. 5

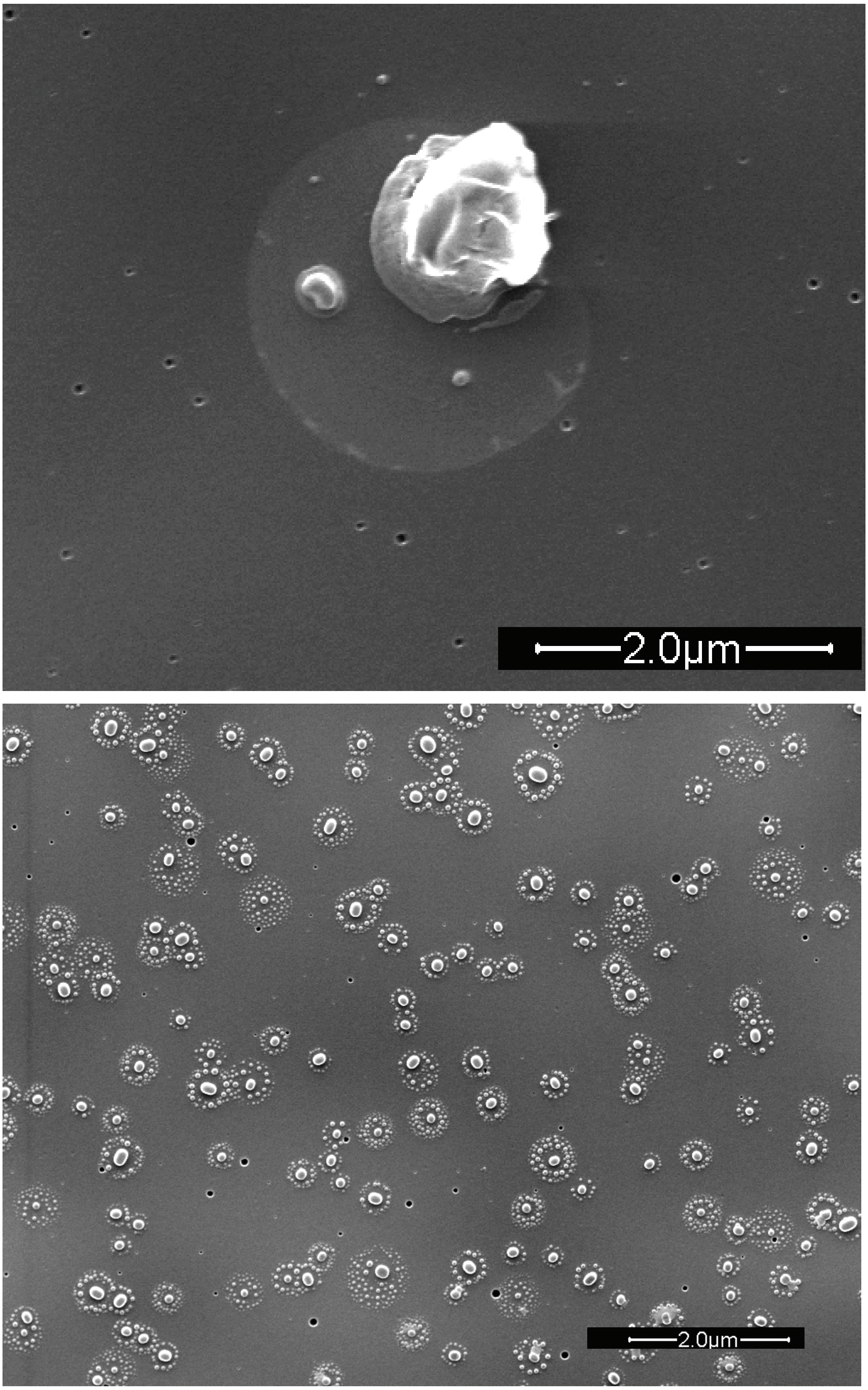


Fig. 6

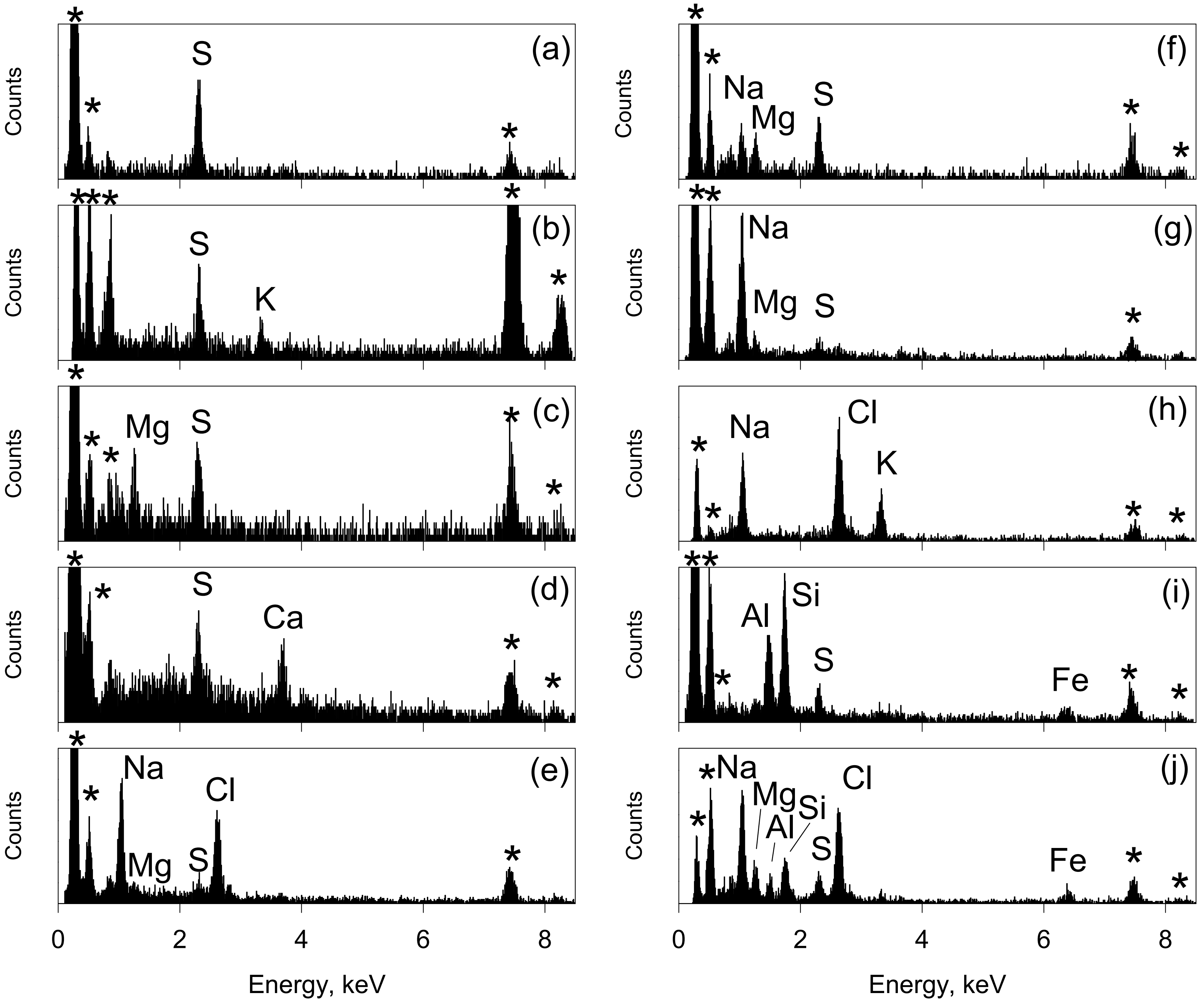

(a)
S
(b)
S
K
(c)
Mg
S
(d)
S
Ca
(e)
Na
Mg
S
Cl
(f)
Na
Mg
S
(g)
Na
Mg
S
(h)
Na
Cl
K
(i)
Al
Si
S
Fe
(j)
Na
Mg
Al
Si
S
Cl
Fe
*
Counts
0
2
4
6
8
Energy, keV

Fig. 7

Fig. 8

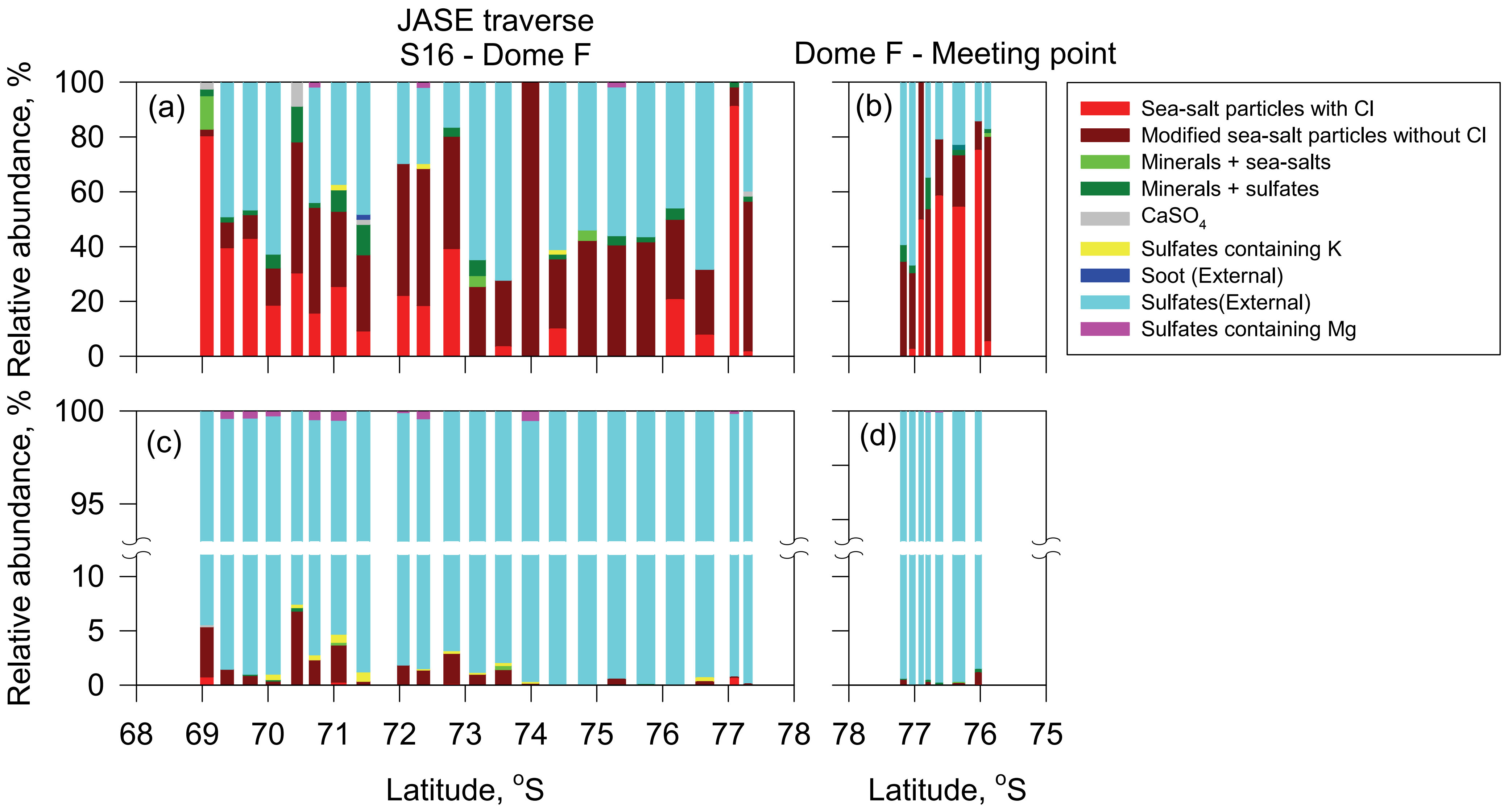
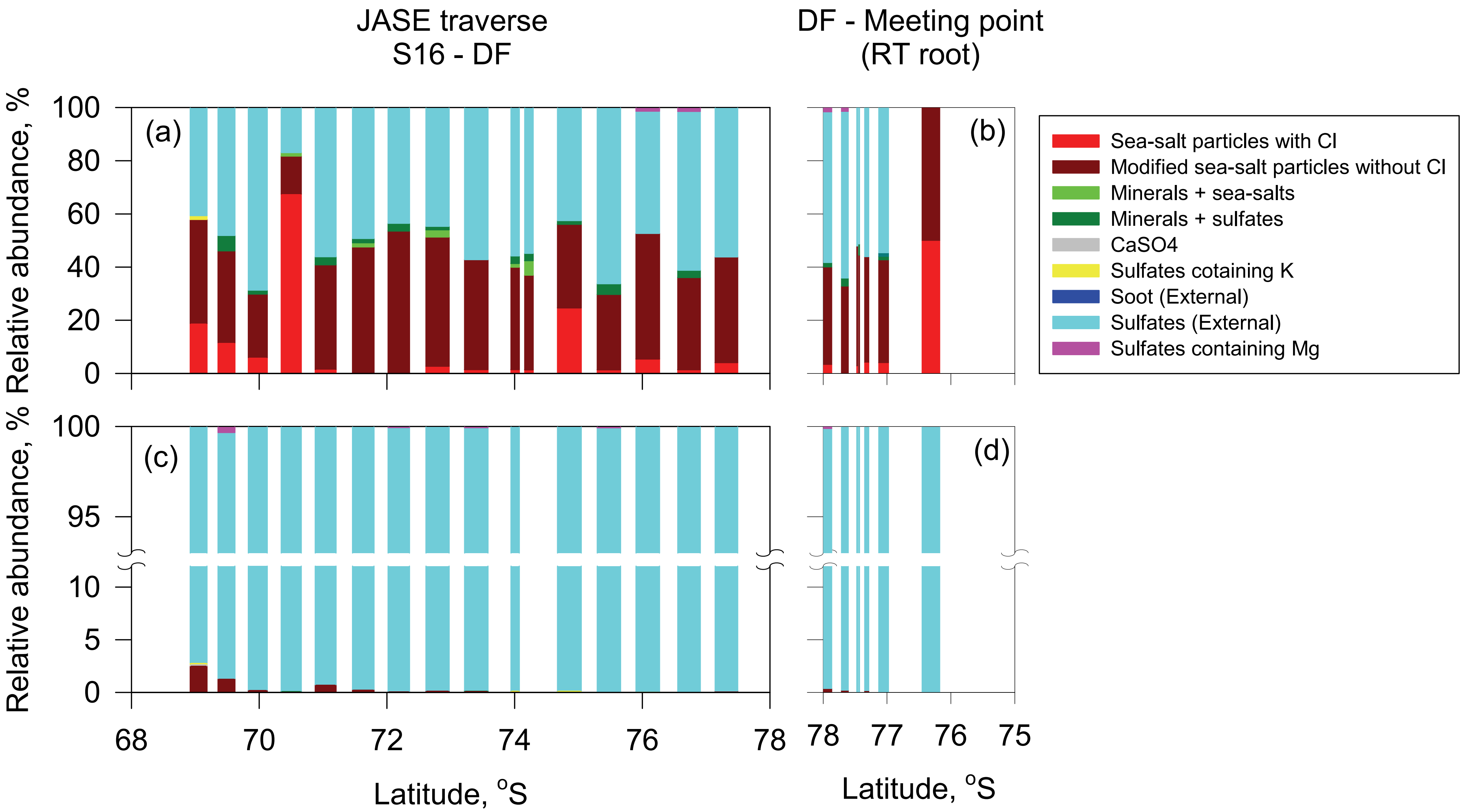

JASE traverse
S16 - Dome F
Dome F - Meeting point
(a)
(b)
(c)
(d)
Relative abundance, %
Relative abundance, %
100
80
60
40
20
0
100
95
10
5
0
68
69
70
71
72
73
74
75
76
77
78
78
77
76
75
Latitude, °S
Latitude, °S
Sea-salt particles with Cl
Modified sea-salt particles without Cl
Minerals + sea-salts
Minerals + sulfates
CaSO$_4$
Sulfates containing K
Soot (External)
Sulfates(External)
Sulfates containing Mg

Fig. 9


JASE traverse
S16 - DF
DF - Meeting point
(RT root)
(a)
(b)
(c)
(d)
Relative abundance, %
Relative abundance, %
100
80
60
40
20
0
100
95
10
5
0
68
70
72
74
76
78
78
77
76
75
Latitude, °S
Latitude, °S
Sea-salt particles with Cl
Modified sea-salt particles without Cl
Minerals + sea-salts
Minerals + sulfates
CaSO4
Sulfates cotaining K
Soot (External)
Sulfates (External)
Sulfates containing Mg

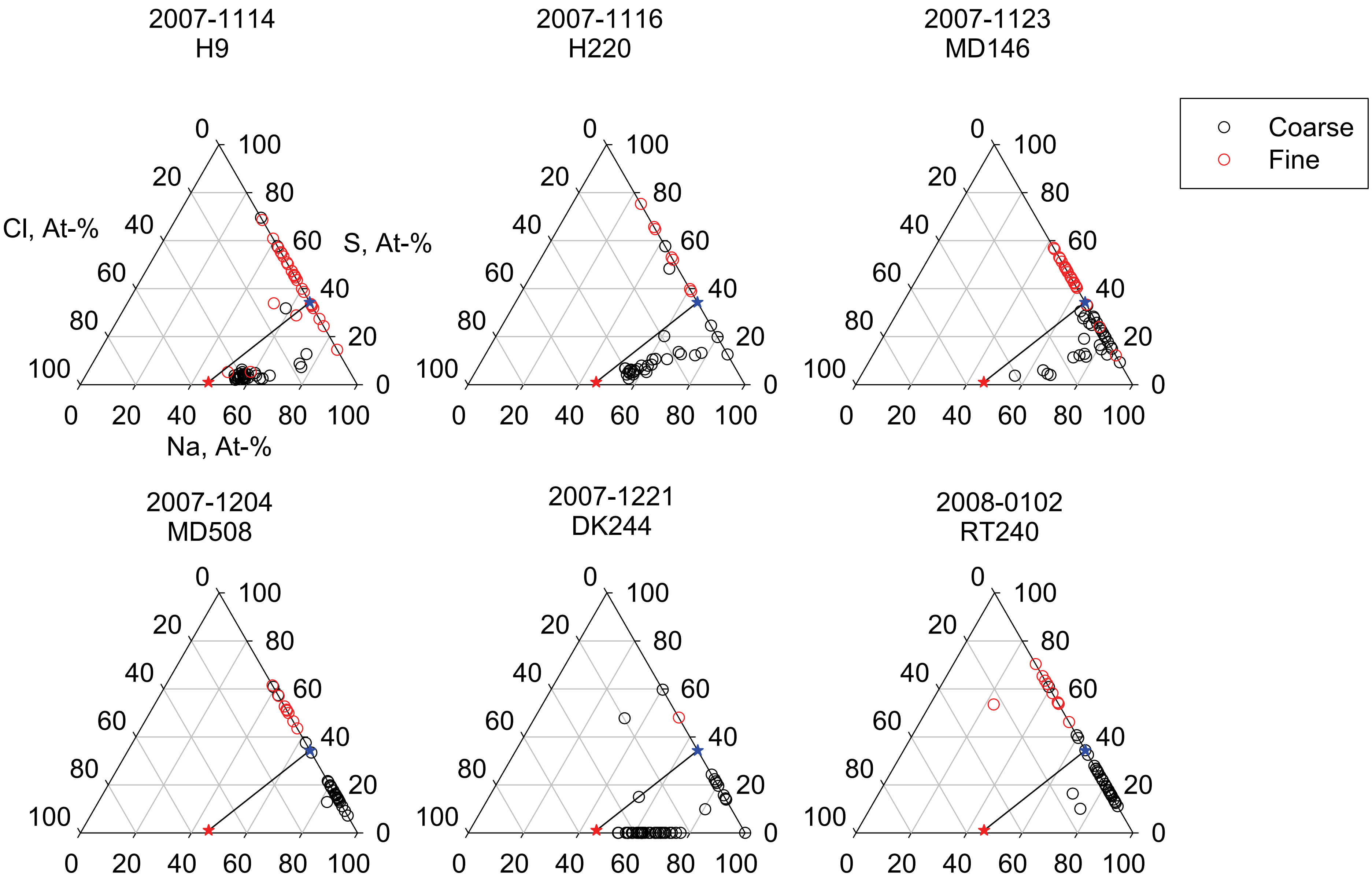

2007-1114
H9
2007-1116
H220
2007-1123
MD146
2007-1204
MD508
2007-1221
DK244
2008-0102
RT240
Cl, At-%
S, At-%
Na, At-%
0
20
40
60
80
100
Coarse
Fine

Fig. 10

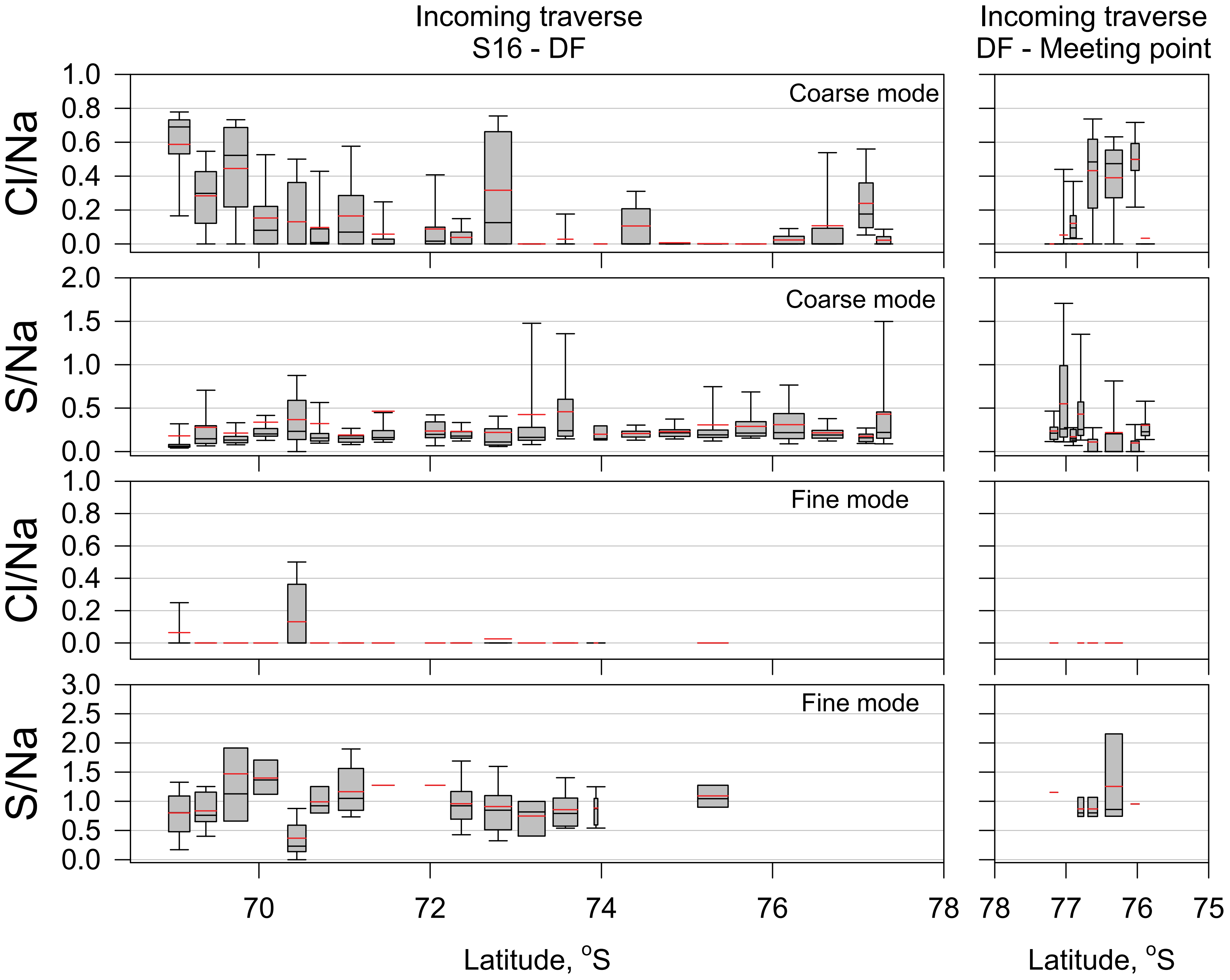

Incoming traverse
S16 - DF
Incoming traverse
DF - Meeting point
Cl/Na
S/Na
Cl/Na
S/Na
Coarse mode
Coarse mode
Fine mode
Fine mode
1.0
0.8
0.6
0.4
0.2
0.0
2.0
1.5
1.0
0.5
0.0
3.0
2.5
2.0
1.5
1.0
0.5
0.0
70
72
74
76
78
78
77
76
75
Latitude, °S
Latitude, °S

Fig.11

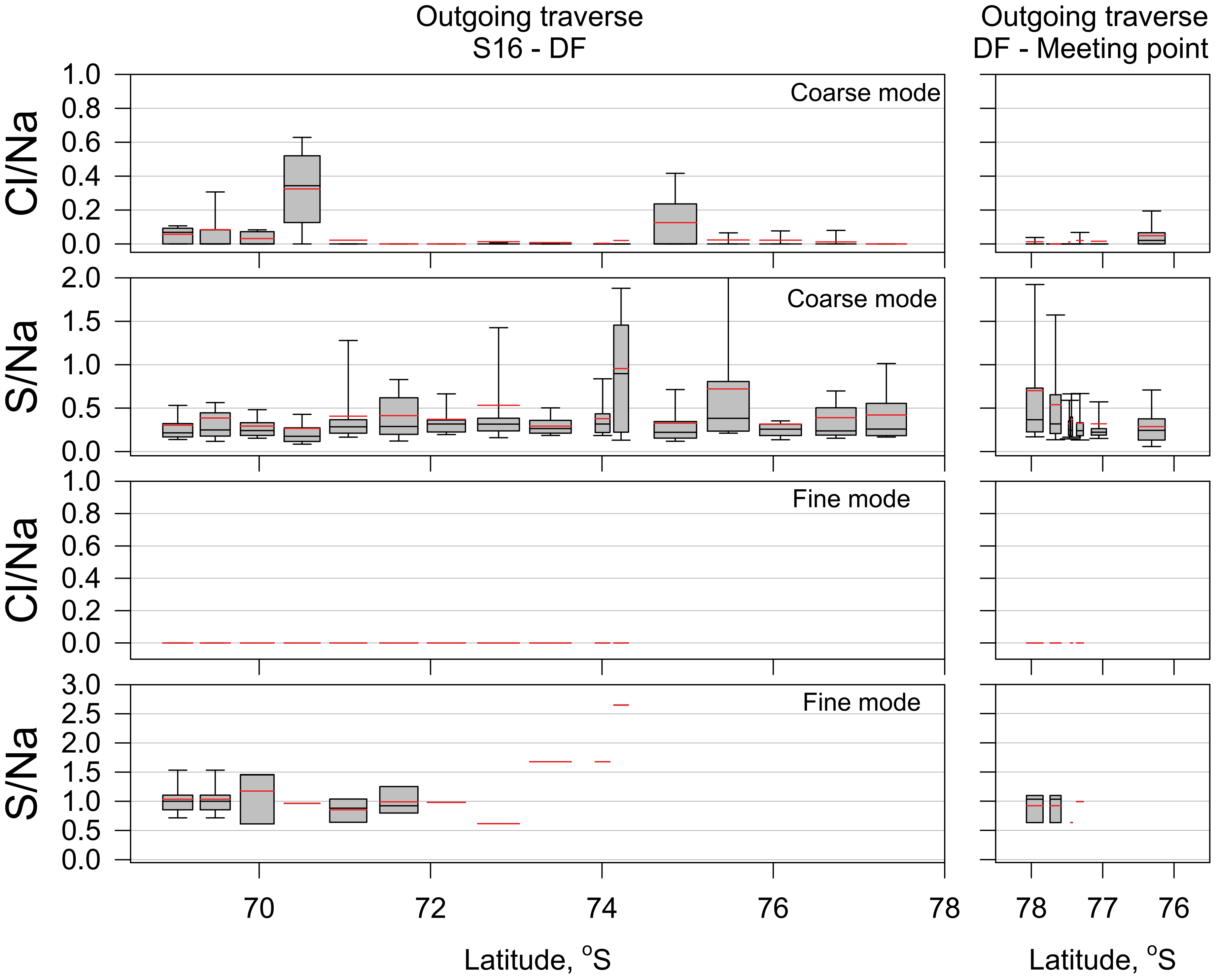

Outgoing traverse
S16 - DF
Outgoing traverse
DF - Meeting point
Cl/Na
S/Na
Cl/Na
S/Na
Coarse mode
Coarse mode
Fine mode
Fine mode
1.0
0.8
0.6
0.4
0.2
0.0
2.0
1.5
1.0
0.5
0.0
3.0
2.5
70
72
74
76
78
77
Latitude, °S

Fig.12

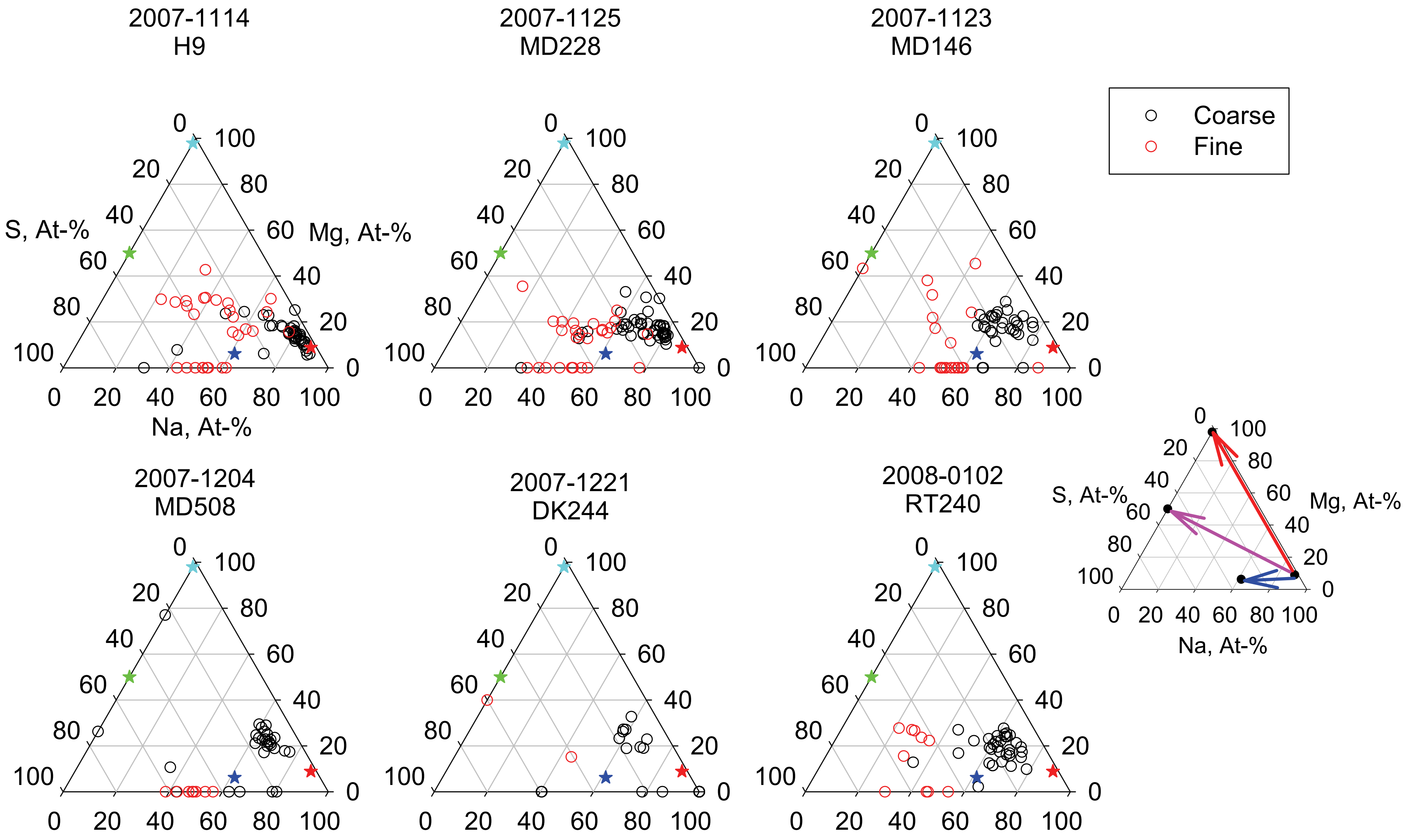

2007-1114
H9
2007-1125
MD228
2007-1123
MD146
2007-1204
MD508
2007-1221
DK244
2008-0102
RT240
S, At-%
Mg, At-%
Na, At-%
0
20
40
60
80
100
Coarse
Fine

Fig.13

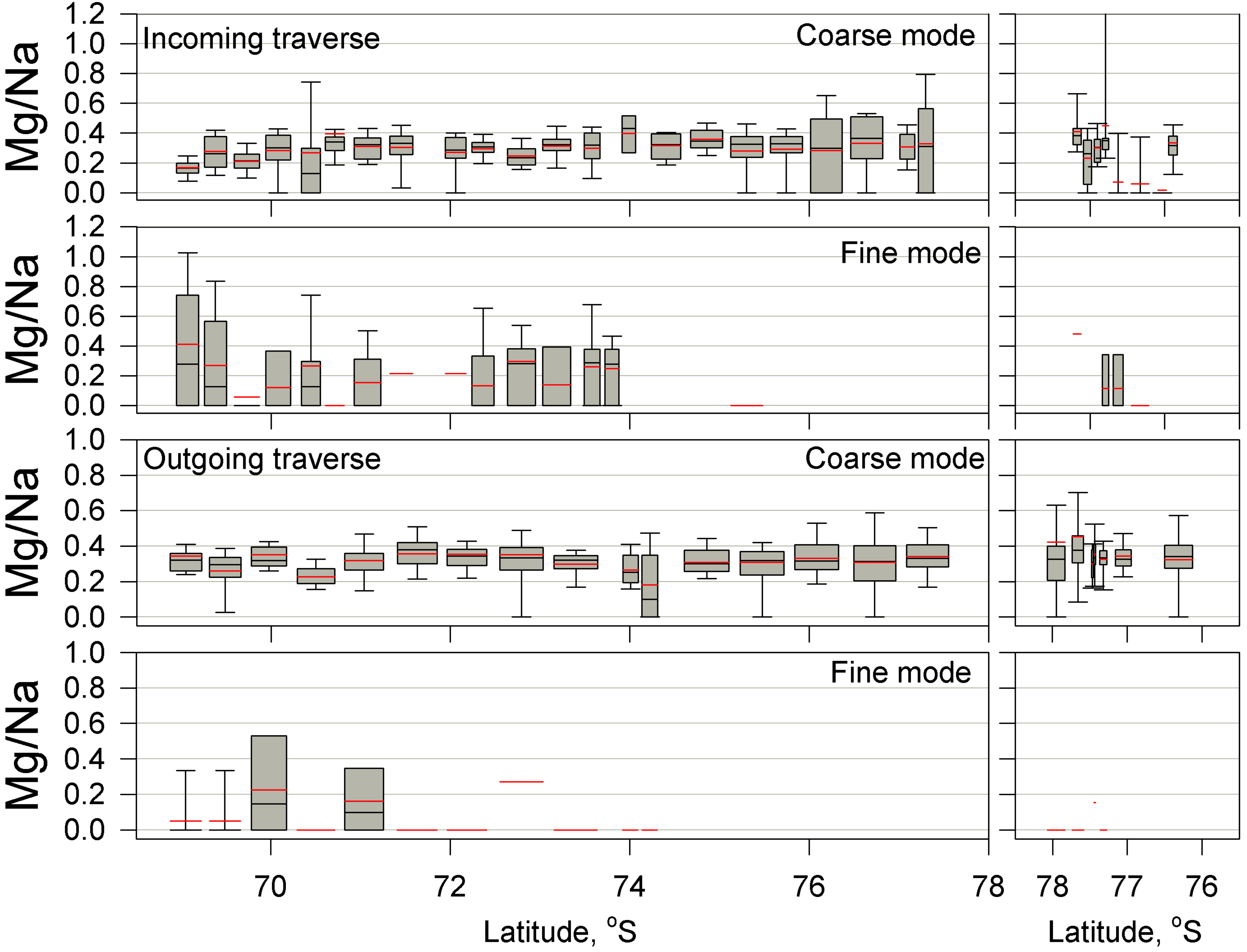

Mg/Na
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Incoming traverse
Coarse mode
Fine mode
Outgoing traverse
Coarse mode
Fine mode
70
72
74
76
78
78
77
76
Latitude, °S
Latitude, °S

fig. 14