

Spatial distributions of soluble salts in surface snow of East Antarctica

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ABSTRACT

To better understand how sea salt reacts in surface snow of Antarctica, we collected and identified non-volatile particles in surface snow along a traverse in East Antarctica. Samples were obtained during summer 2012/2013 from coastal to inland regions within 69°S to 80°S and 39°E to 45°E, a total distance exceeding 800 km. The spatial resolution of samples is about one sample per latitude between 1500 and 3800 m altitude. Here, we obtain the atomic ratios of Na, S and Cl, and calculate the masses of sodium sulphate and sodium chloride. The results show that, even in the coast snow sample (69°S), sea salt is highly modified by acid (HNO₃ or H₂SO₄). The fraction of sea salt that reacts with acid increases in the region from 70°S to 74°S below 3000 m a.s.l., where some NaCl remains. At the higher altitudes (above 3300 m a.s.l.) in the inland region (74°S to 80°S), the reaction uses almost all of the available NaCl.

Keywords: sea salt, modification, sodium sulphate, sodium nitrate, single-particle analysis

1. Introduction

Aerosols are of central importance for atmospheric chemistry and physics (Pöschl, 2005). In the free troposphere, they have a strong influence on direct and indirect radiation effects in the Earth's atmosphere (Andreae, 1995). Some form by the disintegration of bulk material on the Earth's surface (e.g. sea salt and mineral dust), whereas others are produced by chemical reactions (scavenging and loss of gases, aqueous phase reactions) in the atmosphere. The latter are known as secondary aerosols.

In the present (Holocene) climate of Antarctica, various studies have addressed the seasonal concentrations of major

aerosol constituents including SO₄²⁻, CH₃SO₃⁻, NO₃⁻, sea salts (e.g. Na⁺ and Cl⁻) and minor aerosol constituents of minerals and carbonaceous species (e.g. soot and organics) (Kerminen et al., 2000; Legrand et al., 2001; Jourdain et al., 2008; Preunkert et al., 2008; Udisti et al., 2012). To better understand the origins of these constituents and the chemical reactions that occur on aerosol particles, single-particle analyses of Antarctic aerosols have been done (Parungo et al., 1979; Artaxo et al., 1992; Hara et al., 1995, 2005, 2013; Mouri et al., 1999). More recently, Hara et al. (2014) showed that most sea-salt particles in the continental region near the coast were modified with acidic sulphur species such as H₂SO₄ and CH₃SO₃H. In contrast, other, non-sulphurous acidic species (likely HNO₃) contributed markedly to sea-salt modification in inland areas during the traverse.

The same ions (SO₄²⁻, NO₃⁻, CH₃SO₃⁻, Na⁺ and Cl⁻) have also been detected as major components in Antarctic snow precipitation and snowpack (Legrand and Delmas,

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1985, 1986, 1988a, 1988b; Mulvaney and Wolff, 1994; De Angelis and Legrand, 1995; Kreutz and Mayewski, 1999; Wagnon et al., 1999; Isaksson et al., 2001; Suzuki et al., 2002; Delmas et al., 2003a, 2003b; Davis et al., 2004; Dibb et al., 2004; Huey et al., 2004; Iizuka et al., 2004; Fischer et al., 2007). The consistency between the aerosol and snow composition suggests that past aerosols are well preserved in Antarctic snow. However, due to the high volatility of NO_3^- and CH_3SO_3^- (Wagnon et al., 1999; Röthlisberger et al., 2002), melted samples of surface snow, firn and Holocene ice from inland Antarctica contain mainly sodium, chloride and sulphate ions (Legrand and Delmas, 1988a; Legrand and Mayewski, 1997; Petit et al., 1999; Watanabe et al., 2003; Iizuka et al., 2004, 2006; Wolff et al., 2006; Fischer et al., 2007). These ions are considered to come from primary sea salt (sodium chloride) and marine biological activity (methane sulphonate and sulphuric acids) in the Southern Ocean (Legrand and Delmas, 1985, 1988a, 1988b; Legrand et al., 2001; Wolff et al., 2006; Fischer et al., 2007; Jourdain et al., 2008; Preunkert et al., 2008; Udisti et al., 2012). As these soluble aerosols typically travel more than several hundred kilometres from the Southern Ocean to inland Antarctica, with very little aerosol added from the Antarctic ice sheet, the composition of soluble aerosols sampled inland is a good indicator of how secondary aerosols are formed (Legrand and Delmas, 1988b; Kerminen et al., 2000; Delmas et al., 2003a). In addition, inland Antarctica contains many deep ice cores from which one can reconstruct past aerosol fluctuations (Petit et al., 1999; Watanabe et al., 2003; Wolff et al., 2006; Fischer et al., 2007). However, interpretation of the aerosol record requires knowledge of aerosol modification.

In previous studies, aerosol constituents in snow were determined using bulk analysis techniques, mainly ion chromatography. For example, in the present Antarctic atmosphere and snow, Cl^-/Na^+ ratios from ion chromatography are used to infer sea-salt modification (Legrand and Delmas, 1988b). This ratio is lowest during the winter because cyclones frequently carry sea-salt aerosols (Na^+ and Cl^-) from the Antarctic sea to the inland ice sheet (Jourdain et al., 2008; Udisti et al., 2012). The mole ratio is highest in summer, when marine biological activity produces a great deal of sulphuric acid, which then passes into the atmosphere and promotes sulphatisation (Preunkert et al., 2008). In addition, gaseous Cl^- (HCl) likely transports more easily inland than particulate NaCl and Na_2SO_4 .

To obtain the concentrations of salt and acid in snow and ice, we previously proposed the ion-deducing method (IDM) to deduce the salt concentrations from ion concentrations in snow and ice (Iizuka et al., 2008). The method is based on two assumptions about salt-formation priority: (1) sulphate has the highest salt-formation priority due to

vaporisation of HNO_3 and HCl (Legrand and Delmas, 1988b; Röthlisberger et al., 2003) and (2) nitrate has a higher salt-formation priority than chloride (Kerminen et al., 2000). For the Dome Fuji ice core (inland Antarctica), the deduced salt concentrations agreed well with the major salts identified from direct measurements of impurities in ice by Raman spectroscopy (Ohno et al., 2005, 2006).

As another analysis method, we developed a sublimation method capable of collecting several hundred non-volatile particles from a small ice sample at temperatures below -50°C (Iizuka et al., 2009, 2012a). This sublimation method can be applied to surface snow and firn (Iizuka et al., 2012b). By applying scanning electron microscopy and energy dispersion X-ray spectrometry (SEM-EDS) to the particles from the sublimated samples, we can determine each particle's constituent elements and also classify the particle as insoluble or soluble. For salt concentrations, both the combination sublimation-EDS method and the IDM method have a close relationship at depths from the surface snow to 4-m depth in the Dome Fuji region (Iizuka et al., 2012b). However, the relation is less close for Holocene ice of the Talos Dome ice core (Iizuka et al., 2013), which was drilled in a coastal area (Delmonte et al., 2010; Stenni et al., 2011). Specifically, the particles in the Talos Dome ice contain a lot of NaCl according to the sublimation-EDS method. But the IDM method showed that the major salt is Na_2SO_4 without NaCl , due to the Holocene ice having more SO_4^{2-} than Na^+ . This implies that sea-salt sulphatisation proceeds in the coastal region, and the reactant NaCl remains even when enough H_2SO_4 exists to react with the sea salt.

Thus, to clarify how much and where the secondary aerosols form on the Antarctic ice sheet, we can use not only the Cl^-/Na^+ ratio and the IDM model but also single-particle analyses by the sublimation-EDS method. These methods had not yet been applied to a spatial study of single-particle analyses in the surface snow of Antarctica. To evaluate the Cl^-/Na^+ ratio and the IDM model, we collected and identified non-volatile particles in the surface snow from coastal to inland regions of East Antarctica. Here, we obtain the atomic ratios of Na, S and Cl, and calculate the masses of sodium sulphate and sodium chloride in surface snow to determine how much the sea salt in surface snow becomes modified during transport from the coast (north) to inland (south).

2. Sampling site and analytical procedures

The samples came from the traverse route in Queen Maud Land, East Antarctica, by the 54th Japanese Antarctic Research Expedition (Fig. 1). On this campaign, the team collected samples in summer of 2012/2013 while travelling from site S16 ($69^\circ 01' 45''$ S, $40^\circ 03' 01''$ E, 534 m a.s.l.), near

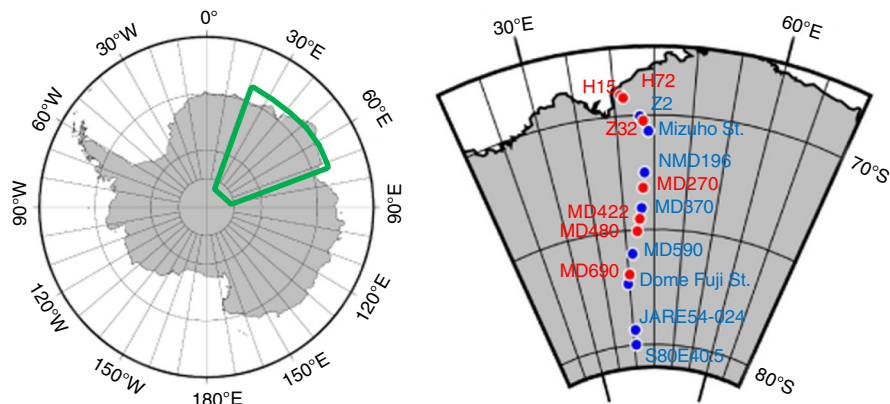


Fig. 1. Region of study and sampling sites in East Antarctica. The green boundary in the left map shows the location in Antarctica. At right, an enlarged region shows locations of snow samples. Blue marks spots where several tens of centimetres were extracted, and red marks spots where only freshly fallen surface snow was extracted. The base map is from GMT free software.

Syowa Station, to inland Antarctica at 80°S and 45°E via Dome Fuji Station (77°19′01″ S, 39°42′12″ E, 3810 m a.s.l.). All sampling sites lie within 69°S to 80°S, and 39°E to 45°E (1022–3803 m a.s.l.). For comparisons, in this area, Suzuki et al. (2002) measured ion concentrations of surface snow during 1999/2000, and Hara et al. (2014) measured single-particle constituents in the atmosphere during 2007/2008.

We collected seven samples of freshly fallen surface snow up to a 5-cm depth. These samples are considered as snowpack from summer precipitation. To compare to precipitation over the past several years, we also collected eight samples of snow cover from the surface to 30- to 80-cm depth. Pits with 30–80 cm depth were dug, and innerwall snow was removed using a cylindrical sampler. As a result, each snow sample represents several years of accumulated snow. After well mixing the snow cover sample in a clean bag, we put the samples into clean plastic bottles. Before their use, these bottles and tools were cleaned in an ultrasonic bath using ultra-pure water in a clean room at the National Institute of Polar Research, Japan. The sample dates, source locations and particle properties are listed in Table 1.

We did laboratory analyses for the major soluble ion concentrations and chemical component analysis of the non-volatile particles. For analysis of major ion concentrations, the ice samples were melted in cleaned bottles and then their concentrations of soluble ions were measured using ion chromatography (Dionex, DX500) following the scheme in Miyake et al. (2009). These major ions include CH_3SO_3^- , Cl^- , SO_4^{2-} , NO_3^- , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . We previously proposed the IDM to determine the concentration of salt compounds for the Dome Fuji ice core (Iizuka et al., 2008). The IDM is based on the assumption that salts form at different rates, in the order (fast-to-slow) of (1) CaSO_4 , (2) other sulphate (Na_2SO_4 and MgSO_4), (3) nitrate

and (4) chloride. In Antarctica, the contribution of NH_4^+ is too small. The excess anions (e.g. Cl^-) over cations exist as acid (Iizuka et al., 2008).

For the component analyses, we pulverise 1 g of snow from each sample and sublimate the snow on a polycarbonate filter with a pore size of 0.4 μm (Advantec, K040A013A) at -50°C using clean, dry air following Iizuka et al. (2009). All filters are coated with platinum for 30 s to a thickness of 10 nm using magnetron sputtering (Vacuum Device, MSP-10). We then analyse the 15 filter samples using a SEM/EDS system (JEOL, JSM-6360LV/JED2201). In this study, each filter yielded several hundred particles exceeding 0.4- μm diameter. Using SEM–EDS at 20 keV, we determine the levels of O, Si, Al, S, Cl, Na, Mg and Ca in the particles. We do not analyse the levels of C and N due to inaccuracies with light elements and because C is a contaminant from the polycarbonate filter. Finally, we assume that Na-containing particles contain sea-salt aerosol.

To determine the sulphate and chloride components, we use the sublimation–EDS method described by Iizuka et al. (2009, 2012a). This method identifies the non-volatile particles and separates the non-volatiles into soluble and insoluble components. Particles containing Si are assumed to have silicate material. Almost all S and Cl in the non-volatile particles are from soluble materials. As the dry air ventilation removes gas materials such as HCl and HNO_3 , and because remnant liquid droplets (H_2SO_4) are unstable under the measurement environment (in vacuum at 25°C), we can assume that any sea-salt modification during the sublimation is negligible (Oyabu et al., 2014). The S and Cl in the non-volatile particles are assumed to be from solid particles such as sulphate and chloride salts (Iizuka et al., 2012a). After considering the possible remaining compounds, we can assume that Na and S in a given particle came from Na_2SO_4 , whereas Na and Cl came from NaCl.

Table 1. Particle sampling sites, their positions and dates

Sample site	Latitude (°S)	Longitude (°E)	Altitude (m)	Distance from the sea (km)	Sampled date	Top (cm)	Bottom (cm)	Particle measured number (N)	Average diameter (μm)
H15	69.07	40.77	1022	132	23 Nov 2012	0	5	505	0.83
H72	69.20	41.08	1185	167	23 Nov 2012	0	5	456	0.87
Z2	70.04	43.15	1924	406	25 Nov 2012	0	80	195	0.79
Z32	70.25	43.55	2060	453	26 Nov 2012	0	5	348	0.72
Mizuho	70.71	44.27	2215	540	27 Nov 2012	0	50	362	0.81
NMD196	72.51	43.64	2845	537	3 Dec 2012	0	50	373	1.05
MD270	73.17	43.35	3063	553	5 Dec 2012	0	5	255	1.13
MD370	74.06	42.98	3338	567	8 Dec 2012	0	50	361	0.91
MD422	74.52	42.62	3431	573	9 Dec 2012	0	5	369	1.06
MD480	75.05	42.17	3537	585	10 Dec 2012	0	5	503	0.83
MD590	76.03	41.13	3684	621	12 Dec 2012	0	50	383	0.89
MD690	76.93	40.12	3754	681	14 Dec 2012	0	5	434	0.80
Dome Fuji	77.32	39.70	3803	714	13 Jan 2013	0	30	461	0.96
JARE54-024	79.36	40.51	3678	890	28 Dec 2012	0	30	348	0.91
S80E40.5	80.00	40.50	3625	944	3 Jan 2013	0	30	367	0.81

Distance from the sea is measured from Syowa Station (69.00°S, 39.58°E). Also shown are the number of measured particles, particle diameters and depth of snow extracted.

For other salts, Ca and S are assumed to come from CaSO_4 , Mg and S from MgSO_4 , Ca and Cl from CaCl_2 , and Mg and Cl from MgCl_2 . A similar assumption is also adapted for atmospheric aerosols (e.g. Hara et al., 2014). If S (or Cl) is found in particles without Na, Mg or Ca, we regard the S- (or Cl-) containing particles as other, unidentified sulphate (or chloride) salts. When a particle has Na, S and Cl, the molar ratio of Na_2SO_4 and NaCl depends on those of S and Cl as follows: If $[\text{Na}] < [\text{S}] + [\text{Cl}]$ (μeq), then $[\text{Na}_2\text{SO}_4] = [\text{S}] / ([\text{S}] + [\text{Cl}]) \times [\text{Na}]$ (μeq) and $[\text{NaCl}] = [\text{Cl}] / ([\text{S}] + [\text{Cl}]) \times [\text{Na}]$ (μeq). If instead $[\text{Na}] > [\text{S}] + [\text{Cl}]$ (μeq), then $[\text{Na}_2\text{SO}_4] = [\text{S}]$ (μeq) and $[\text{NaCl}] = [\text{Cl}]$ (μeq).

The calculated uncertainty of the single-particle number and mass ratios follows the method described by Iizuka et al. (2009) and (2012b) respectively. The uncertainty of the number ratio is based on the assumption that the errors follow the Poisson distribution law. Over all samples, the average uncertainty of the number ratio is 5.2 %. For the mass ratio, the uncertainty is based on the coefficient of variation (CV) for each atomicity ratio, based on the average values and SDs of these 20 measurements. For example, the CVs of Na, S and Cl were 0.40, 0.39 and 0.45, respectively. The average uncertainty of the mass ratio Na_2SO_4 to NaCl is 8.1 % over all samples. For the spherical approximation, the calculated uncertainty for 95 % of the particles is below 0.20. For the ratio of Na_2SO_4 to NaCl, the average value of CV ratio over all samples is 0.281. The uncertainty values (5.1–28.1 %) are almost the same or less than those from ion concentrations measured using ion chromatography (i.e. 5–10 %).

3. Results and discussion

3.1. Chemical characteristics of soluble particles from coastal to inland regions in Antarctic snow

In going from the coast (ca. 1000 m a.s.l.) to inland (ca. 3800 m a.s.l.), the fraction of Cl-containing particles to total particles decreases and the fraction of S-containing particles increases (Fig. 2). This latter fraction remains consistent among all summer and multiyear samples. As most of the particles contain S or Cl, sulphate and chloride salts are major compounds of the non-volatile particles. For such particles having sulphate or chloride salt, Na is the major metal. This result shows that the major compounds of sulphate and chloride salts are Na_2SO_4 and NaCl, respectively.

The particles labelled ‘other’ in Fig. 2 have neither S nor Cl. These other particles are likely to be mainly NaNO_3 (see later discussion), whereas those that contain Si are likely silicate minerals.

From 69°S (coastal region) to 73°S (ca. 3000 m a.s.l.), about half of all salt-containing particles have NaCl. But from 74°S (ca. 3300 m a.s.l.) to 80°S (inland region), most salt-containing particles instead have Na_2SO_4 (Fig. 2). This result is consistent among all summer and multiyear samples. Thus, it suggests that, from the coast to inland, the sea-salt (NaCl) sulphatization reaction (Legrand et al., 1988b) is as follows:



Consider now the ion concentrations at the same locations. Table 2 shows that the major ion species are

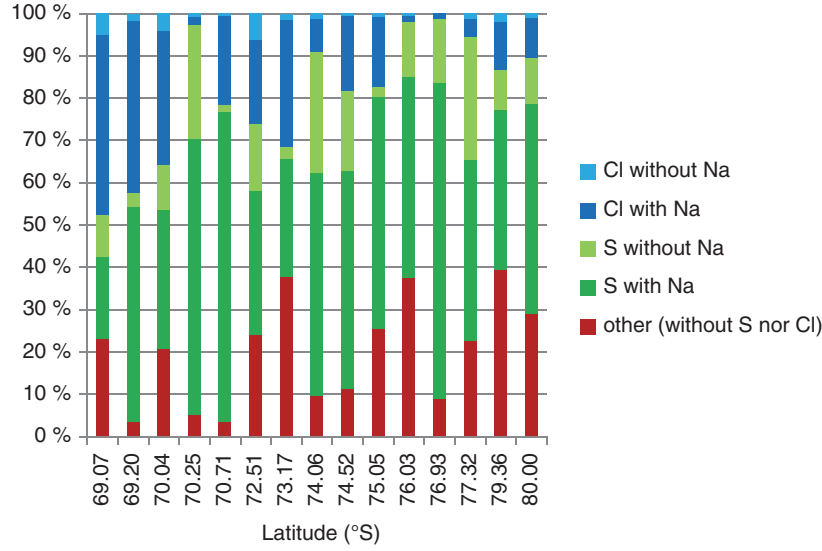


Fig. 2. Elemental distribution of non-volatile particles in surface snow. Each column shows the relative number of particles, at the labelled latitude, having chloride without sodium (light blue), sodium chloride (dark blue), sulphate without sodium (light green), sodium sulphate (dark green) and neither sulphate nor chloride ('other', red).

Na^+ , Cl^- , SO_4^{2-} and NO_3^- from 69°S to 80°S. In agreement with the particle analyses, these ion results show that Na is the major metal and the other three metals are available in minor quantity. Also, the major ions are consistent with the major salts NaCl, Na_2SO_4 and NaNO_3 . The results are also consistent with Hara et al. (2014), who seldom found ammonium salts, instead found that some of the major aerosol compositions on the same traverse route are Na_2SO_4 and NaNO_3 . NaNO_3 is thought to be formed by (Kerminen et al., 2000)



Thus, NaNO_3 comes at the loss of NaCl. Because $\text{Cl}^- + \text{SO}_4^{2-} + \text{NO}_3^- \gg \text{Na}^+$ (Table 2), some of the Cl^- , SO_4^{2-} and NO_3^- form acids (HCl , H_2SO_4 and HNO_3) and some form salts (NaCl , Na_2SO_4 and NaNO_3).

Consider the Cl^-/Na^+ ratio. NaCl is the major component of sea salt, and H_2SO_4 originates from marine biological activity. NaCl and some H_2SO_4 in this area come from the Southern Ocean via the troposphere, whereas the remaining H_2SO_4 and HNO_3 originate from the stratosphere, passing from inland to the coast (Suzuki et al., 2002). The concentration of Cl^- until 70°S (ca. 2000 m a.s.l.) is larger than that of the other two anions (Table 2). In particular, the

Table 2. Ion concentrations (Cl^- , SO_4^{2-} , NO_3^- , Na^+ ; $\mu\text{mol L}^{-1}$) and Cl^-/Na^+ ratio

Sample site	Altitude (m)	Cl^-	SO_4^{2-}	NO_3^-	Na^+	Cl^-/Na^+	Na_2SO_4 (IDM)	NaCl (IDM)
H15	1022	11.50	1.18	1.02	9.69	1.19	1.18	7.33
H72	1185	4.29	0.55	2.25	1.75	2.45	0.55	0.65
Z2	1924	1.61	0.49	0.84	1.21	1.33	0.49	0.23
Z32	2060	0.94	0.57	0.73	0.52	1.80	0.26	0
Mizuho Station	2215	1.40	0.86	1.65	0.83	1.69	0.41	0
NMD196	2845	1.42	0.36	1.29	0.96	1.48	0.36	0.24
MD270	3063	1.54	0.71	2.60	0.83	1.85	0.42	0
MD370	3338	0.76	0.45	1.34	0.32	2.39	0.16	0
MD422	3431	n.a.	n.a.	n.a.	n.a.			
MD480	3537	0.57	0.33	2.40	0.14	4.01	0.07	0
MD590	3684	1.73	0.54	1.51	0.95	1.82	0.47	0
MD690	3754	2.06	0.75	1.90	1.24	1.66	0.62	0
Dome Fuji	3803	2.09	0.80	1.29	1.27	1.64	0.64	0
JARE54-024	3678	1.87	0.83	1.29	0.87	2.16	0.43	0
S80E40.5	3625	1.78	0.73	2.11	0.82	2.17	0.41	0

Na_2SO_4 and NaCl ($\mu\text{mol L}^{-1}$) are from the ion-deducing method (IDM).

Cl^-/Na^+ ratio (1.19) of the $69^\circ 07' \text{S}$ sample is almost the same as the sea-salt ratio (1.18). On the other hand, the Cl^-/Na^+ ratios of the other 14 inland samples are higher (Table 2). This suggests that most sea salts in these inland-snow samples had been modified to Na_2SO_4 or NaNO_3 .

3.2. Sea-salt modification of single particles from coastal to inland regions in Antarctic snow

To further examine sea-salt modification, consider the ternary diagrams of Na, Cl and S atomic ratios in single

particles. The bottom-right diagram in Fig. 3 shows how we interpret the diagrams: the yellow circle marks the sea-salt ratio of the three elements. If sea salt reacts with nitric acid, the plot moves on the purple dotted line to the purple circle. The purple circle means that all Cl is lost and the particle consists only of NaNO_3 . In a similar way, if sea salt reacts with sulphuric acid, the plot moves on the blue dotted line to the blue circle. The blue circle means that the particle consists only of Na_2SO_4 without NaCl. Similarly, the green dotted line and circle represent the reaction that forms $\text{CH}_3\text{SO}_3\text{Na}$. Most of the particle compositions

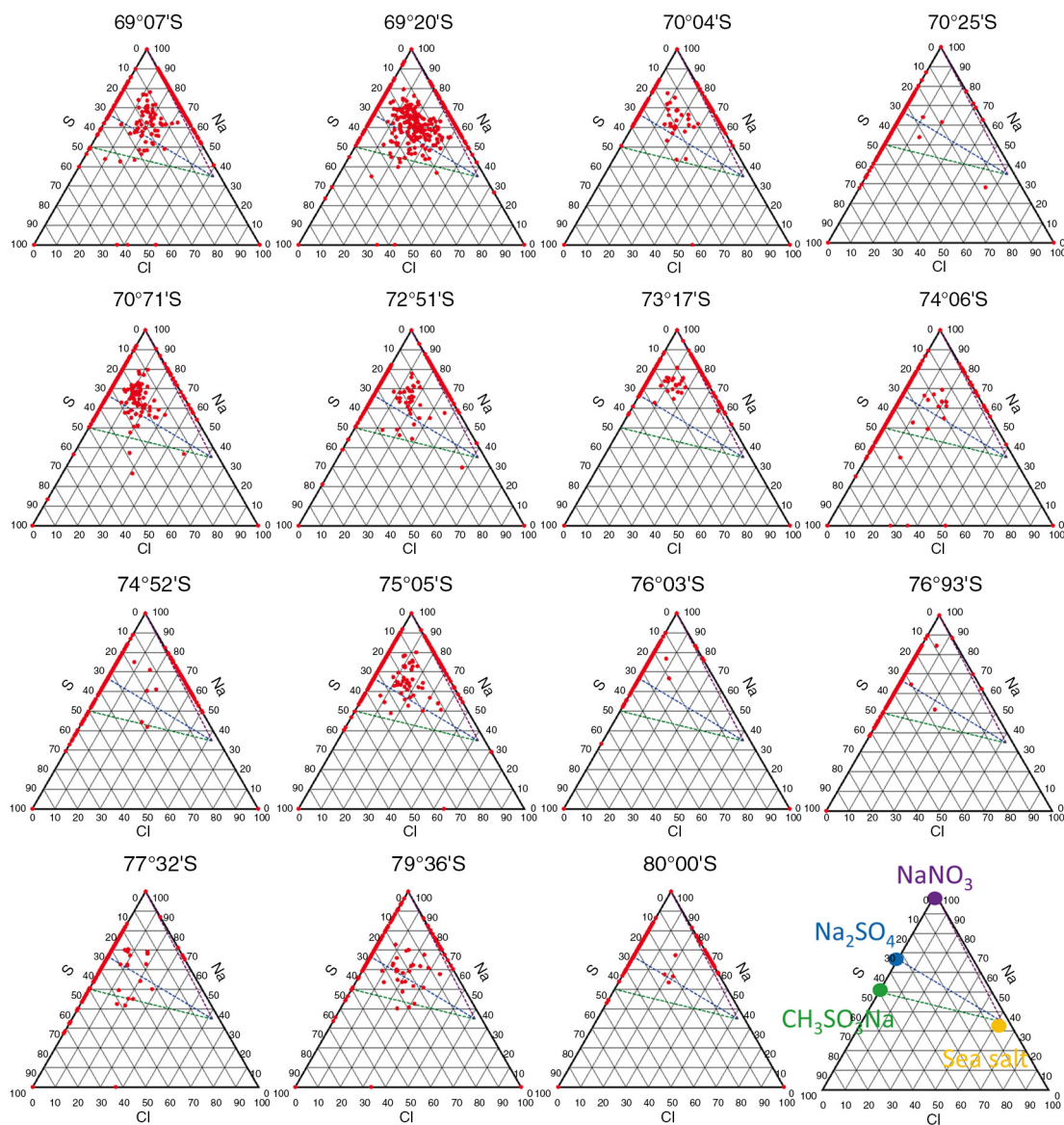


Fig. 3. Ternary plots of Na, Cl and S atomic ratios in non-volatile particles by the sublimation-EDS results. Latitude titles are marked as in Table 1. Yellow, purple, blue and green circles in the bottom-right diagram (right of the 80°S plot) denote the atomic ratios of bulk seawater, wholly Cl-depleted sea-salt particles with nitrates, wholly Cl-depleted sea-salt particles with sulphates and wholly Cl-depleted sea-salt particles with methane sulphonates, respectively.

cluster near the purple or blue dotted lines and circles, indicating that the sea salt reacts to form mainly NaNO_3 and Na_2SO_4 .

The scatter in these ternary diagrams exceeds that from previous aerosol analyses on the same traverse route (Hara et al., 2014). Since only a limited number of particles are actually used for EDS, sample heterogeneity may have contributed to the observed scatter. Otherwise, the increase in scatter likely comes from the larger variability in particle trajectories. The previous aerosols were sampled in a short period and thus trace just one trajectory of sea salt in one air mass. In contrast, the present results come from snowpack, in which the snow composition comes from both snow precipitation and dry deposition after the snowfall. Moreover, the summer samples consist of several snowfall events, each one likely following a different trajectory. So, soluble salts in snowpack are considered to contain a range of aerosol compositions over a duration that includes various air masses.

Almost all particles containing Cl are sea-salt products. Even in the $69^\circ 07' \text{ S}$ sample, sea-salt modification occurs in many particles. In the $69^\circ 07' \text{ S}$ sample, the Cl^-/Na^+ ratio (1.19) is consistent with the sea-salt ratio. Nevertheless, the sea-salt particles in snow may react with acid (HNO_3 or H_2SO_4) and retain the same Cl^-/Na^+ ratio. According to Hara et al. (2014), atmospheric aerosols mainly consist of sea salt in spring and mainly modified sea salt in summer. As the snow was sampled in late November (late spring), there are two possible reasons for the spring–summer difference. One is post-depositional effects may cause the difference; sea salt deposited at the $69^\circ 07' \text{ S}$ site and then acid (dry deposition)

reacted with the deposited sea salt via reactions (1) and (2). As a result, the products are Na_2SO_4 (or NaNO_3) and HCl with the sea-salt ratio of the Cl^-/Na^+ . The second reason is if the two products of Na_2SO_4 (or NaNO_3) and HCl deposit on the same level on snowpack, modified sea-salt particles can be obtained under the sea-salt ratio in bulk snowpack. It also may be a mix of the two reasons.

Below 3000 m a.s.l. (73°S), about half of the sea-salt particles reacted with nitric acid, whereas above 3300 m a.s.l. (74°S), the sea-salt particles instead mainly reacted with sulphuric acid (Fig. 4). Indeed, from 76°S to 77°S (near Dome Fuji at 3700 to 3800 m a.s.l.), almost all sea-salt particles reacted with sulphuric acid. This finding contrasts with Hara et al. (2014), who found that the inland sea-salt particles in atmospheric aerosol instead mainly reacted with nitric acid. The difference between these results may be due to (1), with snow, the acids can continually deposit, thus increasing in amount, and (2), after depositing in or on the snow, the nitric acid may volatilise via the equilibrium reaction $2\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_3$.

Below 3000 m a.s.l. ($<73^\circ \text{S}$), about half of the Na-containing particles partly change, gaining either Na_2SO_4 or NaNO_3 (light blue and purple in Fig. 4). But further inland, above 3300 m a.s.l. (more than 74°S), the fraction with two Na compounds decreases to about one-tenth. Here, almost all Na-containing particles modify fully to either Na_2SO_4 or NaNO_3 (dark blue and purple in Fig. 4) at the expense of NaCl . These results suggest that sea-salt modification occurs progressively on the Antarctic ice sheet as the salt moves inland, with the reactions becoming complete by 3300 m a.s.l. (74°S). As described above, sea-salt particles

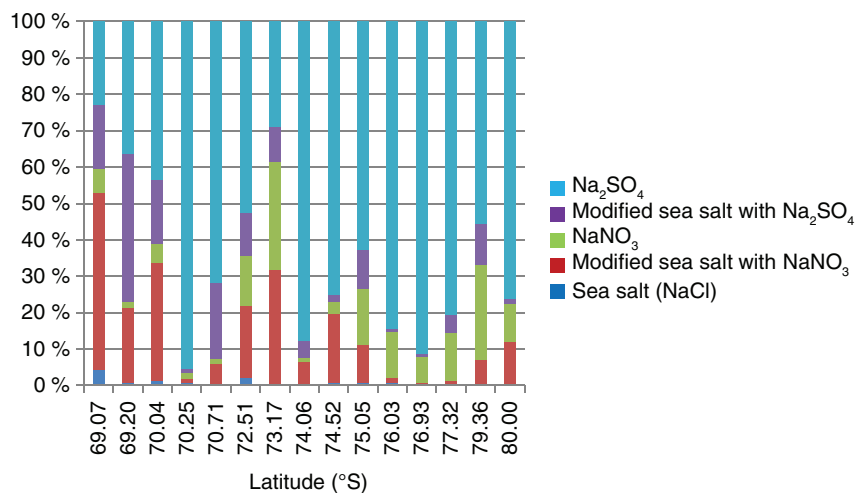


Fig. 4. Number fraction of Na compounds. From the same data as plotted in Fig. 3. Dark blue denotes sea salt. Light blue denotes wholly Cl-depleted sea-salt particles with sulphates and purple denotes partly Cl-depleted sea-salt particles with sulphates. Light green denotes wholly Cl-depleted sea-salt particles with nitrates and brown denotes partly Cl-depleted sea-salt particles with nitrates. The colour order in the data is the same as that in the legend.

mainly reacted with sulphuric acid above 3300 m a.s.l. (more than 74°S). Therefore, Na_2SO_4 is a major soluble salt in snow of the inland region of Antarctica.

Concerning spatial correlations between ion species (Table 2), some are correlated along the entire traverse, and some are not. A plot of Na^+ and Cl^- (not shown) has a strong correlation r^2 , with r^2 exceeding 0.90 ($n = 14$) along the entire traverse. But for Na^+ and SO_4^{2-} , no correlation exists in the coastal region (from 69°S to 74°S), whereas a relatively low correlation of 0.69 ($n = 7$) occurs in the inland area (from 74°S to 80°S). Thus, inland, the correlation between Na^+ and SO_4^{2-} is less than that between Na^+ and Cl^- . These trends agree with previous findings (e.g. Suzuki et al., 2002).

Na^+ and Cl^- are considered as having the same origin (sea salt; $r^2 = 1$), and following eqs. (1) and (2), sea-salt modification increases linearly with the distance from coast to inland. Due to the linear modification through the traverse, the strong correlation between Na^+ and Cl^- remains even after the sea-salt modification on inland

Antarctic snow. On the other hand, in the inland area, Na^+ and SO_4^{2-} are considered as having different origins. Moreover, the ion balance shows $\text{SO}_4^{2-} > \text{Na}^+$, indicating that H_2SO_4 exists. Nevertheless, despite these factors, most Na^+ instead exists as Na_2SO_4 . This finding suggests that using only the ion correlation does not predict the main chemical form in all cases.

3.3. Quantification of sea-salt sulphatisation from coastal to inland regions in Antarctic snow

Due to its importance in the inland region, we now focus on sea-salt sulphatisation by examining the $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratios. With the sublimation–EDS method, we first estimate the mass of Na, Cl and S and then plot the resulting number and mole ratios of $\text{NaCl}/\text{Na}_2\text{SO}_4$. Figure 5 shows that, for each set of compounds, the mole ratio nearly equals the number ratio. The main factors that influence the calculated number and mole ratios are the atomic ratio and diameter of each particle. As the particle diameters

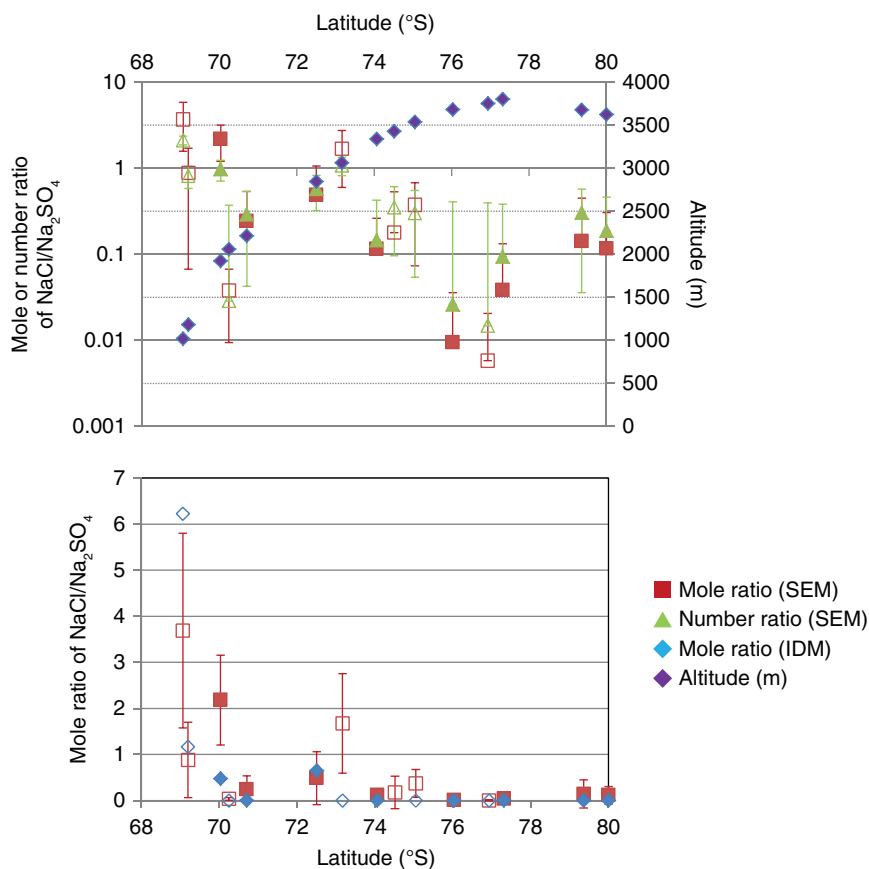


Fig. 5. Mole and number ratios of $\text{NaCl}/\text{Na}_2\text{SO}_4$ along the traverse by the ion-deducing method (IDM) and the sublimation–EDS method. Top plot is logarithmic and also shows the altitude (purple diamonds) along the traverse. The bottom plot is the same, except a normal, linear scale. Non-filled white boxes with coloured frame are for summer snow, whereas the filled coloured boxes mean multiyear snow.

vary, the equality of the two $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratios may be due to the averaging over all the particles on a given filter sample. But regardless of the cause, the result shows that one can use the number ratio to estimate the mole (or mass) ratio of these compounds.

This $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratio is high in the coastal region and low in the inland region. If the sea salt is unmodified, the $\text{NaCl}/\text{Na}_2\text{SO}_4$ ratios of sea salt should be 39.1 and 14.7 for open sea and sea ice origins, respectively (Iizuka et al., 2012b). However, below 2000 m a.s.l. (from 69°S to 70°S), the mole ratio is much lower, ranging from 1 to 10, indicating that $[\text{NaCl}]$ exceeds $[\text{Na}_2\text{SO}_4]$. Then, from about 2500 m a.s.l. (71°S), almost all mole ratios are below 1, indicating that $[\text{Na}_2\text{SO}_4]$ exceeds $[\text{NaCl}]$. So, around 2000 to 2500 m a.s.l. (70°S to 71°S), the major components of soluble salt change from NaCl to Na_2SO_4 . Above 3300 m a.s.l. (more than 74°S), most of the mole ratios are below 0.1, indicating that $[\text{Na}_2\text{SO}_4]$ is more than 10 times higher than $[\text{NaCl}]$. In particular, above 3700 m a.s.l. near Dome Fuji (from 76°S to 77°S), the mole ratio is below 0.01, indicating that $[\text{Na}_2\text{SO}_4]$ is more than 100 times higher than $[\text{NaCl}]$. These results show that sea-salt sulphatisation proceeds inland from the coast, changing 1000-fold between reactant NaCl and product Na_2SO_4 . The lowest ratio, being near the peak of the ice sheet, suggests that the sulphatisation depends on the altitude of the ice sheet. The peak in altitude may be a region of downflow from the stratosphere to the troposphere, a downflow that brings sulphur compounds from the stratosphere (e.g. Delmas and Boutron, 1980; Legrand and Delmas, 1986). Past research shows that winter snow in this region contains more Na^+ and Cl^- , but less SO_4^{2-} than the summer snow (e.g. Iizuka et al., 2004; Hoshina et al., 2014). We did not detect such a winter–summer difference, as the multiyear samples were consistent with the summer samples. This consistency may arise from a post-depositional effect of sea-salt sulphatisation in winter snow. But to test this idea, winter precipitation and surface snow along the same or similar route would need to be analysed.

We previously proposed the IDM to determine the concentration of salt compounds for the Dome Fuji ice core (Iizuka et al., 2008). How well does it work along the present traverse? Table 2 shows $[\text{NaCl}]$ and $[\text{Na}_2\text{SO}_4]$, and Fig. 5 shows the mole ratio of $\text{NaCl}/\text{Na}_2\text{SO}_4$ by the IDM. The IDM assumes that Na^+ more readily combines with SO_4^{2-} than with Cl^- . As a result, NaCl should be negligible where the equivalent $[\text{SO}_4^{2-}] > [\text{Na}^+]$ is inland from 70°S. However, the particle analysis with the sublimation–EDS method detects some NaCl in this inland region. We have found that the sea-salt sulphatisation proceeds in the area below 3000 m a.s.l. (from 70°S to 73°S), yet some NaCl remains, suggesting that the IDM assumption does not apply well to this area. Another area with this same issue is the Talos Dome site. Holocene ice at Talos Dome has a

certain amount of NaCl yet is mismatched with the IDM (Iizuka et al., 2013). Thus, like the Talos Dome site, the IDM method might not accurately determine sea-salt sulphatisation in the coastal region.

On the other hand, the inland area above 3300 m a.s.l. (more than 74°S), the sublimation–EDS method gives $[\text{NaCl}]/[\text{Na}_2\text{SO}_4]$ values below 0.1, indicating less discrepancy between sublimation–EDS and IDM. This means that IDM can be applied inland and suggests that almost all Na^+ does not form NaCl . Similarly, Holocene ice in the Dome Fuji ice core has negligible NaCl , yet closely matches the IDM (Iizuka et al., 2012a, 2012b; Oyabu et al., 2014). Like the Dome Fuji site, the IDM method seems to accurately determine sea-salt sulphatisation in the inland region.

Why is ~ 3300 m a.s.l. (74°S) the threshold latitude at which sea-salt sulphatisation becomes complete? Stohl and Sodemann (2010) suggested a greater likelihood, compared to a subpolar region, of air from the stratosphere reaching the lowest 500 m above the surface in the Antarctic Plateau during summer and autumn. We find that SO_4^{2-} has a minimum near 3300 m a.s.l. (74°S; see Table 2). The minimum likely occurs here because this area lies away from both the coastal source of H_2SO_4 and the stratospheric source in the Antarctic Plateau (above 3700 m a.s.l.) (Suzuki et al., 2003). The sea-salt sulphatisation should proceed in the area from 1000 to 3300 m a.s.l. (69°S to 74°S), due to the high levels of tropospheric SO_4^{2-} , then becoming complete from 3300 to 3800 m a.s.l. (74°S to 80°S), where additional SO_4^{2-} enters from the stratosphere. In fact, the $[\text{NaCl}]/[\text{Na}_2\text{SO}_4]$ values are lowest at the Antarctic Plateau (Fig. 5), where the contribution of stratospheric materials is highest (e.g. tritium concentration as shown in Kamiyama et al., 1989). This additional SO_4^{2-} may accelerate the sea-salt sulphatisation. The 3300 m a.s.l. corresponds to a transition of snow surfaces between smooth (inland plateau type) and rough (katabatic wind zones) (Ageta et al., 1989). The surface snow type may reflect an effective territory of chemicals from the stratosphere. Further study is needed to test this hypothesis; for example, using winter measurements of the area and other areas.

4. Summary

We have analysed the ion concentrations and chemical composition of soluble salts in surface snow on the Antarctic ice sheet within 39°E to 45°E and 69°S to 80°S during summer traverse expedition 2012/2013. Our findings are as follows:

- (1) The Cl/Na ratio (1.19) in the coastal locations was consistent with the sea-salt ratio. Nevertheless, even in the coast sample, the sea salt reacted with acids. This means that even if the Cl^-/Na^+ ratio in bulk

snow equals the sea-salt ratio, the sea-salt particles in snow may react with acid (HNO_3 or H_2SO_4).

- (2) The IDM does not apply to the coastal area from 1000 to 3300 m a.s.l. (from 69°S to 74°S) because sea-salt sulphatation proceeds, and yet a significant amount of NaCl remains. On the other hand, the IDM can be applied in the inland region from 3300 to 3800 m a.s.l. (from 74°S to 80°S) where nearly all Na^+ forms Na_2SO_4 and NaNO_3 compounds.
- (3) We propose a hypothesis for why 3300 m (74°S) is the threshold at which sea-salt sulphatation becomes complete. The sulphatation proceeds from 1000 to 3300 m a.s.l. (from 69°S to 74°S) due to the nearby source of tropospheric SO_4^{2-} and becomes nearly complete from 3300 to 3800 m a.s.l. (from 74°S to 80°S) where there exists a relatively high level of stratospheric SO_4^{2-} . To test this hypothesis, further studies are needed.

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