Spatial and temporal variability of marine-origin matter along a transect from Zhongshan Station to Dome A, Eastern Antarctica

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ABSTRACT

The spatiotemporal distribution pattern of marine-origin matter on the Antarctica ice sheet was used to study variations in the source regions, transport mechanisms and post-depositional influences. We present data on sea salt ions, sulfur components and stable isotopes from surface and snow pit samples collected along the transect route from Zhongshan Station to Dome A during the austral summer in 2012–2013. A general decreasing trend in the accumulation, sea salt ions and sulfur components occurred with increasing distance from the coast and increasing elevation. However, different sources of the marine components, transport pathways and post-depositional influences were responsible for their different spatial distribution patterns. The marine ions in the coastal snow pit varied seasonally, with higher sea salt ion concentrations in the winter and lower concentrations in the summer; the opposite pattern was found for the sulfur compounds. The sea ice area surrounding Antarctica was the main source region for the deposited sea salt and the open sea water for the sulfur compounds. No significant trends in the marine-origin components were detected during the past 3 decades. Several periods of elevated deposition of sea salt ions were associated with lower temperatures (based on $\delta$D and $\delta^{18}O$) or intensified wind fields. In comparison to the sea salt ions, the sulfur concentrations exhibited the opposite distribution patterns and were associated with changes in the surrounding sea ice extent.

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Introduction

Glaciochemical compounds stored in snow and ice on the Antarctic ice sheet can be used as important indicators for tracing global climate changes in the past (Augustin et al., 2004; Marshall, 2003), variations in atmospheric circulation (Delmonte et al., 2010b; Vance et al., 2013) and changes of the source area (Masson-Delmotte et al., 2008; Wolff et al., 2003). Relevant indicators primarily include sea salt ions, dust, stable isotopes, and sulfur components. The sea salt ions originate from the sea ice area or open sea water (Abram et al., 2007; Kurita, 2011; Wolff et al., 2003). Dust originates from bare ground near the seashore or is transported from arid regions in remote Australia (Fischer et al., 2007) or South America (Delmonte et al., 2010a,b). The stable isotopes of water ($\delta^{18}O$, $\delta$D and the second order parameter deuterium-excess ($d$-excess)), which evaporate from lower latitude oceans and are transported southward and deposited in Antarctic snow and ice, can be used as an index for temperature variations at the condensation region (Masson-Delmotte et al., 2008; Xiao et al., 2013) and for

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tracing the source regions (Wang et al., 2012). Marine sulfur components (non-sea-salt sulfate (nssSO₄²⁻) and methanesulfonic acid (MSA)), originating from the oxidation of the emissions of phytoplankton activity, can be used as tracers of the sea ice extent (Abram et al., 2007; Sun et al., 2002) and source regions (Becagli et al., 2004). Moreover, a portion of the deposited nssSO₄²⁻ is from volcanic eruptions and can be used as a reliable reference indicator for dating the ice core (Cole-Dai et al., 2000; Ren et al., 2010) and studying the eruptions’ effects on climate during the past (Gao et al., 2008).

Many traverses from Antarctic coastal areas to interior regions have been executed under the framework of the International Trans-Antarctic Scientific Expedition (ITASE) (Mayewski et al., 2005; Mayewski and Goodwin, 1997) and many valuable glaciochemical data sets have been collected (Becagli et al., 2004; Bertler et al., 2005; Dixon et al., 2013; Kärkäs et al., 2005; Khodzher et al., 2014; Kreutz and Mayewski, 1999; Legrand and Delmas, 1985; Legrand and Mayewski, 1997; Suzuki et al., 2002). The newly available information on the chemical composition of modern snow is helpful in building better models to understand glaciochemical records and the related influencing factors (Dixon et al., 2013; Khodzhier et al., 2014). General information obtained from the traverse route in Eastern Antarctica shows that sea salt ions (Na⁺ and Cl⁻) decreased exponentially with increasing distance from the coast to 200 km inland (Dome Fuji), and sources of Cl⁻ other than sea salt exist in the inland plateau of Antarctica (Suzuki et al., 2002). On the Russian Antarctic Expedition route between Progress Station and Vostok in 2008, Na⁺ exhibited a significant positive correlation with accumulation rate, which decreased as distance from the sea and altitude increased. K⁺, Ca²⁺, and Mg²⁺ concentrations exhibited no significant relationship either with distance inland or with elevation, but peak values existed in the middle section of the traverse (500–600 km). The terrestrial origin of these ions from the Antarctic nunatak areas contributed to their deposition. There were no significant relationships between the sulfate concentrations and distance inland, elevation, slope gradient and accumulation rate either, and nssSO₄²⁻ contributed most to the total sulfate budget (Khodzher et al., 2014). In Western Antarctica, the majority of the non-glaze/dune samples collected along the US ITASE route exhibited similar, or lower, concentrations to those from other studies and comprise a conservative baseline for Antarctic surface snow chemical concentrations (Dixon et al., 2013).

Starting in the 1996/1997 austral summer, the Chinese National Antarctic Research Expedition (CHINARE) has traveled inland along a route from Zhongshan station and in 2005 first arrived at Dome A, the highest point of the East Antarctic ice sheet and 1248 km inland (Fig. 1) (Ding et al., 2011; Hou et al., 2007; Ren et al., 2001, 2010; Xiao et al., 2005, 2013). The accumulation measured via stakes along the route showed that generally decreasing accumulation accompanies increasing distance inland and increasing elevation (Ding et al., 2011). The accumulation rate reached 35 kg/(m²·year) or lower at Dome A (Ding et al., 2011; Hou et al., 2007; Xiao et al., 2008). The surface slope, post-depositional effects and subglacial topography have significant influences on the distribution of accumulation (Ding et al., 2011). The stable isotopes of water (δ¹⁸O and δD) exhibited negative trends with increasing distance inland and elevation (Xiao et al., 2013). Deuterium excess exhibited a positive trend inland, implying a specific transport path that brings moisture into the interior region either from warm, distant moisture sources (high-elevation moisture transport) or from coastal, sea-ice edge areas where

Fig. 1 – Sampling sites along the transect from Zhongshan Station to Dome A. Blue circles and red points were the locations where the surface snow samples were collected on the return trip and used for mercury and major ion analysis, respectively.
large kinetic effects can produce large excesses (low-elevation moisture transport) (Wang et al., 2012; Xiao et al., 2013).

However, presently, no systematic and integrated investigation into the glaciochemical components has been carried out along the entire traverse. Moreover, during the past 8 to 20 years, under the rapid climatic warming scenario, the depositional patterns of the glaciochemical components in Eastern Antarctica have changed greatly (Ding et al., 2015). During the 2012/2013 austral summer field season, a series of glaciochemical samples were collected along the entire traverse route from Zhongshan Station to Dome A. Here, we present the latest glaciochemical data from surficial and snow pit samples and study their spatial and temporal patterns and the related climatic change information.

1. Sampling and analytical procedure

The field expedition of the 29th Chinese National Antarctic Research Expedition (CHINARE) started at Zhongshan Station (69°37′31″S, 76°37′22″E) in December 2012, and reached the Chinese interior research site, Kunlun station, which is located at the highest point of eastern Antarctica, Dome A (80°25′01″S, 77°06′58″E) (Ding et al., 2011; Xiao et al., 2008) in January 2013 (Fig. 1). The distance of the expedition route was 1248 km and the altitude rose from sea level at Zhongshan Station to 4093 m at Dome A. Detailed geographic information on the route and the snow accumulation are listed in Table 1 and have been presented by others (Ding et al., 2011; Hou et al., 2007; Xiao et al., 2008).

In total, 13 snow pits were dug as the expedition route moved inland, and 585 snow or firn samples were collected from the pits. Detailed information on the snow pit sites is shown in Table 1. During the return traverse route, the accumulation rates were measured based on the heights of the stakes along the traverse route and the densities of the surface snow, snow temperatures (at 15 cm depth) and air temperatures (50 cm above the surface), which were measured simultaneously. In total, 66 groups of data were obtained for the entire traverse route (Table S1 in Appendix A. Supplementary data). Moreover, 181 surface snow samples were taken evenly along the route, and 66 samples were selected for trace metal analysis and the other 115 samples for major ions. The sampling containers for all the samples were 250 mL Nalgene low-density polyethylene (LDPE) wide mouth bottles, which were thoroughly acid-cleaned following a strict cleaning procedure (Hong et al., 2000; Liu et al., 2011) at the State Key Laboratory of the Cryospheric Sciences (SKLCS) in Lanzhou and double-sealed in acid-cleaned LDPE bags. All the sampling tools, such as the plastic scraper and knives, were also pre-cleaned prior to leaving for field work. For the snow pits, after the digging step, another twenty-centimeter profile was further peeled off with clean scrapers. All the samples were taken by pushing bottles into the wall of the snow pits, and two samplers were involved following the “clean hands-dirty hands” protocol described in our previous work (Zhang et al., 2012). Details on cleaning and sample handling

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>Location</th>
<th>Altitude (m)</th>
<th>Distance (km)</th>
<th>Depth (cm)</th>
<th>Accumulation (kg/(m²·year))</th>
<th>n</th>
<th>Sampling date</th>
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<td>138.5</td>
<td>20</td>
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<td>210</td>
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<td>172.0</td>
<td>20</td>
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<tr>
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<td>200</td>
<td>121.6</td>
<td>20</td>
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<td>886</td>
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<td>88.0</td>
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<td>976</td>
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<td>33.3</td>
<td>80</td>
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<td>25.4</td>
<td>100</td>
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<td>1248</td>
<td>300</td>
<td>23.5</td>
<td>100</td>
<td>Jan/05/2013</td>
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<td>77°21′11″E</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The accumulation was the mean value of each snow pit calculated based on the dating results. 

n represents the total number of the samples collected from each snow pit.
protocols can be found in the relevant references (Huang et al., 2012; Loewen et al., 2007; Zhang et al., 2012). The surface snow samples were taken by vertically pushing the sampling bottles into the snow surface, and usually no less than 5-centimeter depth was involved for each sample. After sampling, all the samples were double-sealed with clean bags and kept in clean, dark boxes and transported back to SKLCS in frozen status (< −10°C) and stored in a dark refrigerator (−18°C) until further processing.

Before analysis, an approximately 100 mL snow sample (equivalent to a ~40 mL liquid sample) was first aliquoted and transferred into clean bottles and used for major ions, dust and stable hydrogen and oxygen stable isotope analyses. The samples were analyzed immediately after melting in a clean room (1000-class for the room and 100-class for the operating chamber). Cations were analyzed on a Dionex ISC 3000 ion chromatograph (Dionex ISC 3000, Thermo Scientific, USA) using an Ion Pac CS12A column, 20 mmol/L MSA eluent and a cation electrolytically regenerated suppressor (CERS). The anions were analyzed on a Dionex ISC3000 ion chromatograph (Dionex ISC3000, Thermo Scientific, USA) using an Ion Pac AS11-HC column, 25 mmol/L KOH eluent, and an anion electrolytically regenerated suppressor (ASRS). The detection limits, which were defined as 3 times the standard deviation of the baseline noise, were approximately 1 ng/g for all major ions.

The stable isotope (D and 18O) compositions of all samples were analyzed by a liquid-water isotope analyzer (DLT 100, Los Gatos, USA) based on off-axis integrated cavity output spectroscopy (OA-ICOS) at the SKLCS. The isotopic ratios were expressed in per mil (‰) units relative to Vienna Standard Mean Ocean Water (V-SMOW). The accuracies of δD and δ18O measurements were ±0.6‰ and ±0.2‰, respectively.

2. Results and discussions

2.1. Spatial distribution pattern of glaciochemical factors

2.1.1. Accumulation rate

The latest mean annual accumulation rates (2011–2013) were obtained by measuring the heights of the bamboo stakes above the snow surface and the snow densities along the traverse route. In all, 603 groups of accumulation data were collected and shown in Fig. 2. A generally negative trend in accumulation with increasing altitude and distance inland was observed. However, complicated variability was also found in certain specific sections. The accumulation measured at a given location was a combined result of precipitation and post-depositional effects, such as sublimation, drifting snow, etc. The surface slope, wind direction and wind velocity have significant effects on the accumulation values (Ding et al., 2011). According to Ding’s results, the entire 1248 km traverse route was divided into five sections according to their surface slopes and morphological conditions (Ding et al., 2011). Zones 1 to 5 lie in the distance sections 68–202, 202–524, 524–800, 800–1128, and 1128–1248 km, respectively. The latest accumulation data calculated for 2011–2013 showed that the average accumulation in Sections 1 and 2 exhibited higher values (206.9 ± 70.8 and 81.5 ± 52.1 kg/(m²·year), respectively) in comparison with those measured during 2005–2008 (155.2 ± 64.6 and 67.0 ± 54.7 kg/(m²·year)). However, lower accumulations were observed for the inland three sections, and the mean accumulation in Section 3 (49.0 ± 36.1 kg/(m²·year)) was 5 kg/(m²·year) lower than that during 2005–2008 (53.1 ± 44.6 kg/(m²·year)). Section 4 exhibited the largest difference (13 kg/(m²·year), i.e., 62.8 ± 37.0–75.0 ± 52.1 kg/(m²·year)), and Section 5 (32.9 ± 17.2 kg/(m²·year)) was 3 kg/(m²·year).

Fig. 2 – Spatial distribution of the marine-origin glaciochemical components (Na+, Cl−, Mg2+, MSA, and nssSO42−) along the traverse route from Zhongshan Station to Dome A. Accumulation rates measured from both the stakes (gray bars) and the snow pits (black dots with 1 time deviation) and altitude are also shown relative to the distance inland.
lower than the earlier value (35.0 ± 18.3 kg/(m²·year)) (Ding et al., 2011, 2015).

The 13 snow pits were also used to monitor the spatial variations of the accumulation and certify the measured values in situ (Table 1). The mean accumulation rates calculated from the snow pits also showed a general negative trend inland and good correlation with the measured values. The highest accumulation was recorded at the coastal site (268.0 kg/(m²·year), 29-A), and this value shows good consistency with the previously measured value at the LGB69 stake array over the period 1999–2002 (286 kg/(m²·year)) (Ding et al., 2011; Xiao et al., 2005). Significant decreases in accumulation accompanied the increased elevation in the 40–520 km section. The lowest accumulations were detected at the innermost site, Dome A (23.5 kg/(m²·year), 29-M), where the “diamond dust” precipitation could occupy ~7% of the total annual accumulation (Hou et al., 2007), and the lowest snow density (265.6 kg/m³) was also detected at Dome A (Ding et al., 2015). Another site with low accumulation was detected at 690 km (29.7 kg/(m²·year), 29-H). This location is relatively near the DT217 stake array (728 km), and they share the same morphological and meteorological conditions (Ding et al., 2011; Ma et al., 2010). The “hard/soft” snow surface type was found at this location. Low annual mean wind speeds (3.9 m/sec) and high annual mean wind directional constancy (0.91, Ma et al., 2010) have also been recorded. The slope (~350°) was oriented along the prevalent wind direction (northeast). The site contains well-developed wind crusts, and 31% of the DT217 stakes indicate negative accumulation over a 9 year period (Ding et al., 2011). Therefore, it can be deduced that there is strong wind ablation in effect in this area.

2.1.2. Marine ions

Undoubtedly, sea salt is the main source for Na⁺, Cl⁻, and Mg²⁺ ions (Legrand and Mayewski, 1997; Suzuki et al., 2002). In both the surface (Table 2) and snow pit samples, the three ions are highly positively correlated with each other, implying that they are from the same source. However, for the initial section of the transect route (0–160 km inland), the mean concentrations of the three relatively stable chemical ions in the snow pits exhibited higher values than in the surface snow (Fig. 2). This deviation is because the surface snow was collected during the austral summer season, which features a large amount of snowfall (Xiao et al., 2008). Within the regions with higher accumulations, the concentrations of the sea salt ions only represent the mean concentration of a single season. Moreover, the major contribution source of sea salt ions is the region covered in sea ice (Wolff et al., 2003). Therefore, lower areas of sea ice coverage in the summer may also be responsible for the lower sea salt ion concentrations in surface snow. However, for the interior region, which features much lower accumulation rates, the surface snow depth (~10 cm) can represent an entire year’s accumulation; thus, no significant deviation was detected between the two kinds of samples in the inland regions.

Delmas (1992) suggested that sea-salt deposition in polar snow is very high in coastal areas but decreases rapidly inland as a function of elevation rather than distance from the sea. Minikin et al. (1994) found an exponential decrease in Cl⁻ concentrations on the Flichner-Ronne ice shelf, which is essentially flat. These findings indicate that sea-salt concentration variations in coastal areas of Antarctica are dependent both on altitude and distance from the coast. The concentration of Na⁺ in snow is plotted against the distance from Zhongshan Station and altitude. Regression analyses using an exponential formula were performed on these datasets based on the assumption that sea-salt aerosols in the atmosphere were deposited on the ice sheet in proportion with their concentration in the atmosphere, i.e., a first-order removal process (Suzuki et al., 2002). For the mean Na⁺ concentrations in the snow pits and distance inland, the equation was:

\[ y = 59.75e^{-0.0018x} \left( R^2 = 0.66, n = 13 \right) \]  \hspace{1cm} (1)

while with altitude, the equation was:

\[ y = 122.77e^{-0.0007x} \left( R^2 = 0.84, n = 13 \right). \]  \hspace{1cm} (2)

Statistically, the half-decrease distance of sea-salt aerosols deposited on the ice sheet estimated using the exponential term from Eq. (1) is approximately 400 km. Similarly, the concentration of sea-salt aerosols deposited on the ice sheet decreases by half with every 1000 m of increasing altitude.

<table>
<thead>
<tr>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>MSA</th>
<th>Cl⁻</th>
<th>nssSO₄²⁻</th>
<th>Altitude</th>
<th>Distance</th>
<th>δD</th>
<th>Accumulation</th>
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<td>0.972 *</td>
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<td>0.987 *</td>
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<td>0.930 *</td>
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<td>−0.069</td>
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<td>Accumulation</td>
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* * The data is significantly correlated at p < 0.01.

MSA: methanesulfonic acid; nssSO₄²⁻: non-sea-salt sulfate.
The Cl\(^-\)/Na\(^+\) concentration ratio ([Cl\(^-\)/[Na\(^+\)], W/W) was calculated to illustrate the sources and mechanisms influencing the deposition of sea-salt aerosols (Suzuki et al., 2002). For the surface snow samples, the relationship between Cl\(^-\) and Na\(^+\) can be expressed as:

\[
[\text{Cl}^-] = 1.99 \left[\text{Na}^+\right] + 16.04 \left( R^2 = 0.97, n = 115 \right).
\]

The good fit \((R^2 = 0.97, n = 115)\) and the slope of the linear regression \((1.99, \text{very close to the Cl}^-/\text{Na}^+ \text{ ratio in sea water} (1.81 \text{ W/W}) (\text{Broecker et al., 1982})\) suggest that sea salt is the dominant source of both Na\(^+\) and Cl\(^-\) along the transect route. The positive intercept indicates that additional chloride sources may also be important sources of Cl\(^-\) (Becagli et al., 2004). For the snow pit samples, the initial section \((0-600 \text{ km})\) featured a weight ratio of the two ions \((2.08 \pm 0.17)\) close to that of bulk sea water. However, an elevated ratio \((2.93 \pm 0.44)\) was detected for the interior part of the transect route, implying that other sources or post-depositional effects played significant roles in the deposition of sea salt aerosols.

Previous researchers have noted that the volatile chloride compound HCl can evaporate after initial deposition of sea salt on the surface snow, especially at sites with low accumulation rates (Traversi et al., 2004). Re-deposition of chloride at sites with higher accumulation rates can increase these areas’ chloride concentrations. Drifting snow, especially at sites with high down-slope wind velocities, may be another reason for the increase of the Cl\(^-\)/Na\(^+\) ratio at the inland sites along the transect (Ren et al., 2010; Traversi et al., 2004). In addition, Cl\(^-\) species also come from volcanic and anthropogenic activities via the stratosphere or upper troposphere (Dixon et al., 2013; Legrand and Mayewski, 1997). Along with the increase in the mean ratio of the two ions, the standard deviations of the ratios also increased, supporting the speculation that there are other mechanisms influencing the deposition of Cl\(^-\) in the interior plateau area (Li et al., 2014).

Variations in marine productivity can be investigated through the temporal behavior and spatial distribution of two sulfur cycle components (nssSO\(_4^{2-}\) and MSA) (Becagli et al., 2004). NssSO\(_4^{2-}\) was calculated using the following equation:

\[
\text{nssSO}_4^{2-} = \left[\text{SO}_4^{2-}\right]_{\text{total}} - 0.253 \left[\text{Na}^+\right]
\]

where, 0.253 is the sea water sulfate/sodium ratio (W/W). NssSO\(_4^{2-}\) and MSA arise from the atmospheric oxidation of dimethylsulfide (DMS), which is produced by phytoplankton activity in the ocean (Saltzman, 1995). MSA is only produced by biological marine life (Castebrunet et al., 2009; Legrand and Saige, 1991), whereas nssSO\(_4^{2-}\) also arises from other sources, such as volcanic and anthropogenic emissions and crustal erosion (Cole-Dai et al., 2000). Nevertheless, in Antarctica, the biogenic source of nssSO\(_4^{2-}\) is dominant, especially in summer (Udisti et al., 1999). Indeed, the main contribution to the sulfate budget is from nssSO\(_4^{2-}\), which constitutes approximately 95% of the total sulfate. This value is similar to the ratio at Dome C (95%) (Traversi et al., 2004) and higher than that measured at Hercules Névé (75%) (Traversi et al., 2004) and Talos Dome (88%) (Becagli et al., 2004).

Unlike the sea salt ions, no significant deviations were detected in the two sulfur components between surface snow and snow pit samples along the transect route (Fig. 2). The differences between the seasonal production of sea salt and sulfate ions may be the main cause. During austral summer, larger open sea water areas around the Antarctic continent can cause larger production of DMS and subsequently greater deposition of nss-SO\(_4^{2-}\) and MSA on the surface snow (Castebrunet et al., 2009).

Spatially, decreasing trends of both sulfur ions, together with their flux values, were detected in the initial 200 km (snow pits 29-A to 29-C), implying that the adjacent ocean contributed to the sulfate deposition. In the 200–466 km section (29-D to 29-F), increasing trends in the sulfur component concentrations accompanied the decreases in accumulation (Fig. 2); however, no significant trend was detected for the flux values. Complicated variability in the sulfur compositions in the 500–900 km section (29-G to 29-J) were detected, and higher (including the highest) concentrations were discovered in this section. The low accumulation rates and strong post-depositional effects in this section may be the primary causes (Cui et al., 2010; Ding et al., 2011). In the innermost section of the transect route (29-K to 29-M), higher mean concentrations of the sulfur compounds in snow pits were discovered. However, the flux values exhibited consistent values, implying that the increase in the concentrations was mainly caused by the decrease in the accumulation (Fig. 2).

The MSA fraction is defined as the ratio between the MSA content and the total biogenic oxidized sulfur: MSA / (MSA + nssSO\(_4^{2-}\)). This ratio is dependent on a sampling station’s latitude, altitude, and distance from the sea (Becagli et al., 2004). The mean MSA fraction value of the entire traverse is 0.16 ± 0.09 (W/W), and this value is lower than the values of Victoria Land (0.22 (Udisti et al., 1999) and the circum-Antarctic oceans, where a mean MSA fraction of approximately 0.3 (W/W) was measured, with values up to 0.5 (W/W) (Berresheim, 1987; Pszenny et al., 1989). However, this ratio was higher than that at Talos Dome (0.08 W/W) and Dome C (0.05 W/W) (Becagli et al., 2004). Spatially, the mean ratio measured at coastal sites (29-A to 29-F) is 0.23 ± 0.01 (W/W), slightly lower than the circum-Antarctic oceans, and the ratio decreased to 0.10 ± 0.05 (W/W) for the innermost sites (29-K–29-M). This coastal-inland pattern could be explained by considering a roughly constant regional biogenic nssSO\(_4^{2-}\) content, which, in plateau and semi-plateau sites, was strongly affected by long-range transport contributions, such as volcanic H\(_2\)SO\(_4\) inputs or arrivals of marine air masses from lower latitudes and characterized by lower MSA/nssSO\(_4^{2-}\) ratios (due to the higher temperatures in the source areas) (Becagli et al., 2004; Legrand and Pasteur, 1998). Moreover, the mean MSA fraction ratio measured at Dome A is 0.10 (W/W), twice as high as that of Dome C. According to Wang’s diagnostic results, Dome A had a more southern moisture source region in comparison with Dome C (Wang et al., 2012), and the higher MSA fraction ratio at Dome A may be more evidence supporting this speculation.

2.1.3. δ\(^{18}\)O and δD

The stable isotopes (δ\(^{18}\)O and δD) measured in Antarctic snow and ice have been widely used to quantify past changes
in polar temperatures, and the second-order parameter (d-excess), calculated with the following equation:

\[ d\text{-excess} = \delta D - 8 \times \delta^{18}O. \]  \hspace{1cm} (5)

Eq. (5) has also been used to track the origin of the moisture (Kurita, 2011; Masson-Delmotte et al., 2008; Wang et al., 2012). At the global scale, the \( \delta D \) and \( \delta^{18}O \) values of precipitation samples are correlated, with a mean meteoric water line slope of 8. This is a result of the average ratio between the fractionation factors of D and \( ^{18}O \). The deuterium excess strongly reflects kinetic fractionation processes, such as evaporation, condensation on ice crystals, or droplet re-evaporation (Helsen et al., 2006; Masson-Delmotte et al., 2008).

In this study, both series of \( \delta^{18}O \) and \( \delta D \) values from surface snow and snow pit samples were used to study the variations of the isotopes and the influencing factors (Fig. 3). In comparison with Xiao’s results (Xiao et al., 2013) from surface snow along the same traverse in 2007–2008, our data showed elevated \( \delta D \) values (-321.69‰ ± 63.38‰ versus Xiao’s -326.27‰ ± 58.78‰) and \( \delta^{18}O \) values (-40.95‰ ± 8.13‰ versus Xiao’s -42.72‰ ± 7.81‰). Spatially, both isotopes in the surface snow samples exhibit decreasing trends with increasing distance inland (accompanied by increasing elevation), with mean \( \delta \)-distance slopes of -18.15‰/100 km for \( \delta D \) and -2.37‰/100 km for \( \delta^{18}O \). We also obtained mean \( \delta \)-altitude gradients of -7.14‰/100 m for \( \delta D \) and -0.93‰/100 m for \( \delta^{18}O \). These values were consistent with the Antarctic average value of (-7.2‰ ± 0.1‰)/100 m for \( \delta D \) (Masson-Delmotte et al., 2008). For the snow pit samples, the mean \( \delta \)-altitude gradient is -8.40‰/100 m for \( \delta D \) and -1.11‰/100 m for \( \delta^{18}O \). In comparison with the surface snow samples, the snow pit mean values exhibited much stronger gradients.

The relationship between \( \delta^{18}O \) and \( \delta D \) values in the surface snow samples was

\[ \delta D = (7.78 \pm 0.04) \delta^{18}O - (3.10 \pm 1.75) \left( R^2 = 0.99, n = 115 \right) \]  \hspace{1cm} (6)

and the relationship in the snow pit samples was:

\[ \delta D = (7.60 \pm 0.09) \delta^{18}O - (10.77 \pm 3.82) \left( R^2 = 0.99, n = 13 \right) \]  \hspace{1cm} (7)

This strong linear relationship is a good test of the quality of our sampling and analytical procedures, because any sample evaporation is expected to produce a deviation from the meteoric water line (Xiao et al., 2013). The local \( \delta D/\delta^{18}O \) ratios are 7.78 and 7.60 for the surface samples and snow pit samples, respectively, both of which are lower than that of the Global Meteoric Water Line (GMWL). For the surface snow samples, the ratio is similar to earlier studies on Antarctic snow from other sectors of Antarctica, which featured mean values of approximately 7.75 (Masson-Delmotte et al., 2008). The ratio of the snow pit samples was lower than the surface snow samples, suggesting more intense distillation processes.

![Graph](image_url)  

**Fig. 3** – Spatial distribution of \( ^{18}O \) isotope (\( \delta^{18}O \)), D isotope (\( \delta D \)) and deuterium excess (d-excess) values of surface snow and snow pit samples versus the distance inland from Zhongshan Station to Dome A.
or post-depositional effects occurred after the deposition of the snow (Helsen et al., 2006). However, Xiao’s results on the surface samples along the same transect route during 2007–2008 found a lower ratio (7.5 ± 0.1) than our result (Xiao et al., 2013).

The air temperature ($T_{\text{air}}$) (50 cm above the snow surface) and the snow layer temperature ($T_{\text{snow}}$) (15 cm below the snow surface) values were also measured simultaneously with the collection of the snow samples. The δD values exhibit a strong positive correlation with the temperatures in the snow layer ($R = 0.91, p < 0.01, n = 58$) and the air temperatures ($R = 0.88, p < 0.01, n = 58$). For δ18O, the correlations with the snow layer temperatures ($R = 0.92, p < 0.01, n = 58$) and air temperatures ($R = 0.89, p < 0.01, n = 58$) were also significant (Table 3). Along our traverse, the δD and δ18O values are highly correlated (99.9% significance level) with the surface snow and air temperatures via the following linear relationships (Fig. 4):

$$\delta D = (10.59 \pm 0.76) T_{\text{air}} - (71.31 \pm 18.53) \quad (R^2 = 0.77) \quad (8)$$

$$\delta D = (10.26 \pm 0.64) T_{\text{snow}} - (54.82 \pm 16.95) \quad (R^2 = 0.82) \quad (9)$$

$$\delta^{18}O = (1.37 \pm 0.09) T_{\text{air}} - (8.56 \pm 2.27) \quad (R^2 = 0.79) \quad (10)$$

$$\delta^{18}O = (1.33 \pm 0.08) T_{\text{snow}} - (6.47 \pm 2.05) \quad (R^2 = 0.84). \quad (11)$$

In our results, the δD-temperature slopes are much higher than the average values for Antarctica ([(6.34‰ ± 0.09‰)/°C], Adélie Land (approximately 6.0) (Lorius and Merlivat, 1975), the same route calculated by Xiao (6.5) (Xiao et al., 2013) and along the Trans-Antarctic traverse (6.14) (Qin et al., 1993). This difference was mainly caused by the relatively higher snow and air temperatures measured during the austral summer expedition. Lower annual mean temperatures would cause lower slopes.

The deuterium excess varies from −3.38‰ to 15.12‰ in our dataset, and this variation range is much smaller than Xiao’s results (Xiao et al., 2013). However, consistent with Xiao’s result, a step change was observed in the deuterium excess as a function of either distance to the coast or latitude. This step change is characterized by lower values (on average 4.64‰ ± 3.47‰) for elevations below ~2750 m and higher values (6.99‰ ± 4.21‰) for elevations above ~2750 m (Fig. 3). For the Dome A region, the mean deuterium excess value in the surface snow is 12.98‰ ± 2.14‰ (the mean value for the Dome A snow pit 29-M is 16.74‰ ± 2.90‰), and this value is lower than Xiao’s result (20.96‰ ± 2.83‰) (Xiao et al., 2013) and Masson-Delmotte’s results for Dome A surface snow (18.1‰) (Masson-Delmotte et al., 2008). However, this value is slightly lower than Vostok (15.1‰) (Eyrkin et al., 2002) and higher than Dome C (8.8‰) (Stenni et al., 2010) and EPICA Dronning Maud Land (EMDL) (4.7‰) (Stenni et al., 2010). Higher deuterium excess values usually indicate warmer (more northerly) moisture source regions (Masson-Delmotte et al., 2008). Therefore, the increasing trend of deuterium excess inland means that the moisture source region for the interior area of Eastern Antarctica should be more northerly. According to Wang’s diagnostic result (Wang et al., 2012), the main moisture sources for Dome A are located primarily in the Indian Ocean, approximately 46 ± 4° S, much more southerly than the sources of the Dome F, Dome C, Vostok and EMDL sites. Cold air flow from the Antarctic interior over the warm ocean surface and near the sea ice boundary can lead to strong kinetic fractionation over a large gradient in relative humidity, which can produce very high deuterium excess levels (Kurita, 2011). This may be responsible for the higher deuterium excess values in the Dome A region (Wang et al., 2012).

### 2.2. Temporal variations of the glaciochemical components

One coastal snow pit (29-A) (Fig. 4a) and an interior snow pit (29-L) (Fig. 4b) were selected to study the temporal variations in chemical compositions and the associated influences. Snow pit 29-A is located 40 km from the sea edge and can be considered to be a marine-influenced area. Snow pit 29-A contains ~3 years of snow deposition with a mean accumulation rate of 268 kg/(m²·year) (Fig. 4a). The seasonal variations were mainly traced using deuterium isotopes and sea salt ions (Na⁺, Cl⁻, and Mg²⁺). Generally, higher concentrations of sea salt ions in winter snow layers and lower concentrations in summer were detected (Fig. 4a). From this, we speculate that the main sources for the sea salt ions in the coastal area are from the sea ice regions surrounding the Antarctic continent (Wolff et al., 2003). Opposite variation trends were simultaneously detected for the two sulfur compounds: higher concentrations in summer layers and lower concentrations in winter layers. Areas of open water are the main source of the (DMS), which eventually oxidizes into MSA and nssSO₄²⁻ in the atmosphere (Becagli et al., 2004). MSA is only produced by biological marine life (Legrand and Saigne, 1991), and the biogenic nssSO₄²⁻ is the dominant

| Table 3 – Correlation matrix of the measured snow temperature, air temperature, distance, altitude along the traverse route and stable isotopes from the surface snow samples. |
|------------------|------------------|------------------|------------------|------------------|------------------|
| Snow temperature| 1                | −0.952*          | 0.907*           | 0.917*           | −0.947*          |
| Air temperature  | 1                | −0.928*          | 0.880*           | 0.891*           | −0.900*          |
| Distance         | 1                | −0.943*          | 0.949*           | 0.953*           | −0.913*          |
| δD               | 1                | 0.999*           | 0.999*           | 0.953*           | −0.913*          |
| δ¹⁸O             | 1                | 0.999*           | 0.953*           | 0.953*           | −0.913*          |
| Altitude         | 1                | 0.999*           | 0.953*           | 0.953*           | −0.913*          |

* The data is significantly correlated at p < 0.01.
fraction in Antarctica, especially in summer (Saltzman, 1995; Udisti et al., 1999). The peak values of the sea salt ions (Na⁺, Cl⁻, and Mg²⁺) during the study period were detected in winter of 2011 in association with the lowest temperature (deduced from the lowest deuterium isotopic composition), and this may be related to the larger sea ice extent during colder periods (Wolff et al., 2003). As for the two sulfur compositions, the peak values were found in summer of 2011, and the high values may also be associated with the large sea ice extent in the previous winter (Fig. 5). A larger sea-ice cover around the Antarctic coast is considered to be a positive factor for enhanced phytoplanktonic growth and thus higher DMS production (Sakshaug and Skjoldal, 1989). We detected a simultaneous occurrence of sea salt ions and sulfur components in the surface snow dated to the end of 2012. Higher values of sea salt ions in the summer snow layer may be associated with intensified wind speed and longer durations with strong winds in the coastal area (Fig. 5). Moreover, drifting snow can redistribute the different concentrations of sea salt and can also account for such an irregular distribution.

For the interior snow pit (29-L), a longer period of marine records was obtained and dated back to the mid-1970s (Fig. 4b). Dating of the snow pit was accomplished following the synthesis methods with seasonal variations in the sea salt ions and the stable isotopes of water and was verified by accumulation and the occurrence of the Pinatubo volcanic signature (Li et al., 2009, 2014). Overall, no significant trends in the marine-origin components were detected for the entire period recorded by the snow pit (Fig. 4b). Na⁺, Mg²⁺, and Cl⁻ showed high correlations with each other (0.92 for Na⁺ and Mg²⁺, 0.90 for Na⁺ and Cl⁻, 0.89 for Mg²⁺ and Cl⁻, and p < 0.001, n = 100 for all), implying that they mainly originated from sea salt sources even for the most interior location. The sodium ion concentrations exhibited a significant negative correlation (−0.75, p < 0.001, n = 100) with the δD values, showing that the temperature has a prominent influence on the deposition of

Fig. 4 – Vertical distribution of the marine components and δD values in (a) the coastal snow pit 29-A and (b) the interior snow pit 29-L. The horizontal dotted line indicates the dating results, and the Pinatubo volcanic event is shown in the nssSO₄²⁻ values. Shaded areas in (b) show the locations of the peak marine ions with the numbers L1–L10.
the sea salt ions (Wolff et al., 2003). The two sulfur components also exhibited high correlation (0.50 for nssSO$_4^{2-}$ and MSA, p < 0.001, n = 100), indicating that marine sources were the primary sources of these components.

During the recorded period, several peak values (L1–L10, with concentration higher than the average plus one times standard deviation, Fig. 4b) of marine components were detected. The peak sea salt values were usually accompanied by lower δD values, implying that lower temperatures were associated with the elevated concentrations, and this relationship may be related to the enlarged sea ice area. The larger sea ice extent (SIE) in 2012 may be responsible for the L1 sea salt peak (Fig. 5). Besides that, the intensified wind may also be responsible for the enhanced sea salt ions. L3 showed another peak value on sea salt, and the intensified wind speed and longer duration of strong winds in 2007 may be partially responsible. However, in periods with higher temperature, decreased sea salt ions and increased sulfur ions may be associated with decreased sea ice coverage (Li et al., 2014). L2 showed the peak values for nssSO$_4^{2-}$ and MSA, which occurred simultaneously with higher δD values and lower sea salt ion (Na$^+$, Mg$^{2+}$, Cl$^-$) concentrations. This L2 depth was dated to 2009, which featured higher temperatures measured at Zhongshan Station (Fig. 5). L6 exhibited the highest nssSO$_4^{2-}$ values of the whole snow depth, as well as a high MSA value. This layer was dated to 1992 by the identification of the Pinatubo volcanic signature (Li et al., 2009; Zhou et al., 2006), and there is a good correlation between the depths of the volcanic signal in the 29-L and 29-M snow pits (not shown). Moreover, the δD values at this depth exhibited good correlations with the measured temperature values.

3. Conclusions

Sea salt ions, marine-originated sulfate ions and stable isotope ratios of surface snow and snow pit samples collected along the transect route from Zhongshan Station to Dome A during the austral summer field season in 2012–2013 were presented. Accumulation generally decreased with increasing distance inland and increasing elevation. Large fluctuations were found in certain specific sections (700 km). Comparisons with previous results showed higher accumulation rates in the coastal regions and lower accumulation rates in the interior. The spatial distribution pattern of the sea salt ions exhibited lower concentrations inland, implying that the sea ice area was the main source region. The inland elevated Cl$^-$/Na$^+$ ratio showed that other sources of chloride exist other than sea salt in the interior region or that post-depositional effects affected the deposition of chloride. Unlike the sea salt ions, the sulfur compounds did not exhibit significant inland decreases. The different sources of the nssSO$_4^{2-}$ and MSA and different transport mechanisms may be the dominant influencing factors. The decreased MSA/(MSA + nssSO$_4^{2-}$) ratio inland may imply that more northern sources dominate the deposition of the sulfate in the interior region via longer distance transport. Compared with the water isotopes from the surface snow samples along
the same traverse route, our data exhibited higher values than Xiao’s results from 2007–2008. However, a δD/δ18O ratio that was higher (closer to the GMWL) than the former result was detected. For the Dome A region, higher δ-excess values than Vostok, Dome C and EDML sites were found, indicating that a more southerly moisture source may exist for Dome A or that the source is the sea ice boundary, where very high deuterium excesses can be produced.

Seasonal variations in the marine ion concentrations of the coastal snow pit showed higher sea salt ion concentrations in winter and higher sulfate compound concentrations in summer, indicating that the surrounding sea ice extent was the main source of the sea salt deposition, and that the open sea water was responsible for the load of the sulfate compounds. Longer temporal variations in the marine ions in the interior 29-L snow pit showed that the sea salt ions have a strong negative correlation with the stable isotopes of water, suggesting that lower temperatures are associated with increases in the sea salt deposition via enlarged sea ice extent and vice versa. However, higher sulfate concentrations usually occurred simultaneously with higher temperatures, demonstrating that lower SIE was helpful for the production of sulfate components.

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Appendix A. Supplementary data

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References


