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Inconsistent relationships between major ions and water stable isotopes in Antarctic snow under different accumulation environments

Yu Hoshina [a, b, *], Koji Fujita [a], Yoshinori Iizuka [c], Hideaki Motoyama [d, e]

[a] Graduate School of Environmental Studies, Nagoya University, Chikusa-ku, Nagoya 464-8601, Japan
[b] Now at National Institute for Environmental Studies, Tsukuba, Ibaraki 305-8506, Japan
[c] Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan
[d] National Institute of Polar Research, 10-3 Midori-cho, Tachikawa-shi, Tokyo 190-8518, Japan
[e] SOKENDAI (The Graduate University for Advanced Studies), Tokyo 190-8518, Japan

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ABSTRACT

Major ions, stable oxygen isotopes ($\delta^{18}O$), and accumulation rates are analyzed using high temporal resolution data from shallow ice cores and snow pits from East and West Antarctica. Seasonal cycles of major ions and $\delta^{18}O$ are well preserved at sites with an accumulation rate threshold of >100 kg m^{-2} a^{-1} and calm wind conditions. The seasonal cycle is unclear at sites with high wind speeds, even if the accumulation rate is greater than the threshold. To eliminate the influences of different source regions on major ion and $\delta^{18}O$ signals in ice cores, we calculate correlation coefficients between annually averaged major ion concentrations and $\delta^{18}O$, and then compare these with accumulation rates and other geographical variables such as latitude, elevation, and distance from the coast. We find that accumulation rates are highly correlated with elevation and the 10-m snow temperature, and that major ions and $\delta^{18}O$ are negatively correlated at low accumulation sites in inland Antarctica. Negative correlations could reflect inconsistent accumulation due to a large inter-annual variability in the accumulation rate. The results show that the relationships between major ions and $\delta^{18}O$ may not reflect climatic signatures, and could be a result of the unique characteristics of this arid environment.

1. Introduction

Deep ice cores from inland Antarctica have contributed to a better understanding of global paleoclimate. Water stable isotopes in ice cores can be used as proxies for in situ and moisture source temperatures (Petit et al., 1999; Johnsen et al., 2001; Uemura et al., 2012). Major soluble ions are widely used as proxies of past climate, including ions from sea salt (Na^+ and Cl^-), which are thought to be a proxy for sea ice extent (e.g., Wolff et al., 2006; Fischer et al., 2007). Shallow ice cores from humid environments, where the accumulation rate is more than 300 kg m^{-2} a^{-1} (e.g., Fernandoy et al., 2010), provide high temporal resolution paleoclimate information on regional and/or global scales. In coastal regions, variations in the concentrations of $CH_3SO_3^-$ and non-sea-salt (nss) SO_4^{2-} are used as proxies for marine biological activity, which has been shown to vary with sea ice extent during the Holocene (Curran et al., 2003; Sneed et al., 2011).

Recent advances in analytical technologies have enabled ice core researchers to analyze polar ice cores at a high temporal resolution on annual to seasonal time scales (Steig et al., 2005; Iizuka et al., 2006; de Angelis et al., 2013). However, minimum temporal resolutions are constrained by the sampling interval and the annual accumulation rate.

Deep ice cores covering several glacial cycles, such as Vostok, Dome C, and Dome F, have been drilled in arid environments, where the accumulation rate is less than 50 kg m^{-2} a^{-1} (e.g., Johnsen et al., 2001; EPICA, 2004; Masson-Delmotte et al., 2011; Uemura et al., 2012). It is well known that the original isotopic (and thus temperature) signals are smoothed by isotopic diffusion in firn and ice (Johnsen, 1977; Pol et al., 2010), but it is not well understood how surface snow changes over time after deposition. Recently post-depositional alteration of water stable isotopes in surface

* Corresponding author. National Institute for Environmental Studies, Tsukuba, Ibaraki 305-8506, Japan.
E-mail address: hoshina.yu@nies.go.jp (Y. Hoshina).

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snow has been studied using in situ data (Ekaykin et al., 2002; Hoshina et al., 2014) and simulations (Neumann and Waddington, 2004; Town et al., 2008). Studies of the post-depositional alteration of major ions have shown that gaseous ions (Cl^-,NO_3^-, and $CH_3SO_3^-$) tend to be lost by volatilization from the upper firn to the atmosphere (Wagnon et al., 1999; Delmas et al., 2003a). By comparing three ice cores around Law Dome, Curran et al. (2002) showed that $CH_3SO_3^-$ from summer layers could relocate to winter layers. Additionally, chloride from sea salt is replaced by sulfate after deposition by transportation from the ocean toward inland areas (Delmas et al., 2003b; Iizuka et al., 2012).

It is difficult to obtain high temporal resolution data from polar ice cores drilled in extremely arid environments. Because of insufficient understanding of post-depositional alteration, it is also unclear whether the interpretation of chemical signals in coastal (high accumulation) ice cores can be applied to cores retrieved from low accumulation sites in central Antarctica. Previous studies dealing with post-depositional alteration and the validity of major ions as climate proxies have focused on individual sites rather than discussing spatial variations (e.g., Curran et al., 2002; Göktas et al., 2002; Karlöf et al., 2005). In this study, we consider how accumulation rates constrain the temporal variation of chemical and isotopic signals, and affect the relationship between major ions and $\delta^{18}O$ (and thus temperature) preserved in Antarctic snow.

2. Data and methods

We use major soluble ion concentrations ($CH_3SO_3^-$, Cl^-,NO_3^-,SO_4^{2-}, and Na^+) and $\delta^{18}O$ collected from three snow pits and seven shallow ice cores widely distributed across East and West Antarctica (Fig. 1). The periods analyzed are limited to between 1966 (or later) to the years in which each pit or core was collected (Table 1). The three snow pits (DF, DK, and MP), dug in the summer of 2007 by the Japanese Swedish Antarctic Expedition (JASE) (Fujita et al., 2011; Iizuka et al., 2012; Hoshina et al., 2014), were sampled at 0.02 m intervals (or 0.18–0.25 year intervals) (Hoshina et al., 2014) and were dated using crust layers and variations in Na^+ and Cl^-/Na^+ (Hoshina et al., 2014).

Two of the ice cores were collected by the Japanese Antarctica Research Expedition (JARE) at a coastal site in Dronning Maud Land; H72 was collected in 1993 (Nishio et al., 2002; Suzuki et al., 2005) and YM85 was collected in 2002 (Takahashi et al., 2009). These cores were dated by variations in $CH_3SO_3^-$ (H72; Suzuki et al., 2005) and $CH_3SO_3^-$, NO_3^-, and $nssSO_4^{2-}$ (YM85; Takahashi et al., 2009). Sampling intervals in the H72 and YM85 ice core were 0.04–0.06 m (0.10 years) and 0.02–0.06 m (0.16 years), respectively (Suzuki et al., 2005; Takahashi et al., 2009). Both cores preserved seasonal records of major ions due to their high accumulation rates (128–306 kg m^{-2} a^{-1}). We also use sub-annual records from five ice cores retrieved from West Antarctica (Fig. 1) by the United States International Trans-Antarctic Scientific Expedition (US ITASE; Dixon et al., 2004; Steig et al., 2005). These ice cores were dated using variations in $nssSO_4^{2-}$ (Steig et al., 2005; Mayewski and Dixon, 2013), and the accumulation rates and sampling intervals were 120–470 kg m^{-2} a^{-1} and 0.082 m (0.03–0.09 years), respectively.

To analyze how geographical and climatic settings affect chemical signals preserved in snow, we use accumulation rate data compiled from stake measurements every 2 km along the JARE traverse route (Fig. 1) for the period 1993–2010 (Motoyama et al., 1995, 2002, 2008; Shiraiwa et al., 1996; Azuma et al., 1997; Furukawa et al., 2002; Kameda et al., 2007; Saito et al., 2007) along with snow density data (349–427 kg m^{-3}) (Sugiyama et al., 2012). We also use 10-m snow temperature data from the JARE traverse route and US ITASE sites (Satow and Watanabe, 1992; Nishio et al., 2002; Dixon, 2007).

It is possible that the chemical components used in this study were modified during transport from their origin to the site of deposition; however, water stable isotopes from precipitation correlate well with air temperature at the sites at seasonal to

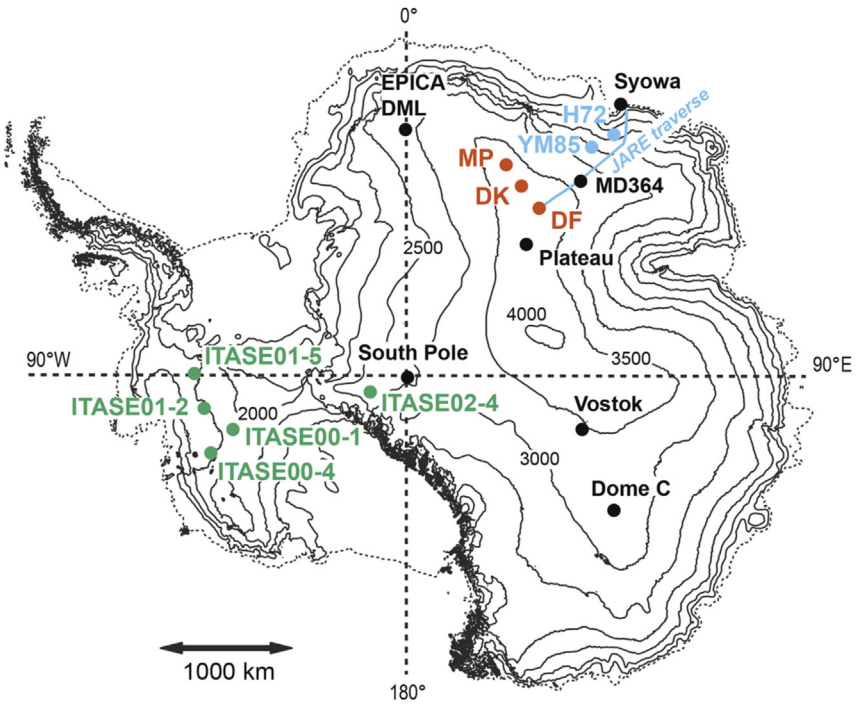

Fig. 1. Locations of ice cores and snow pits used in this study. Red, blue, and green circles denote JASE snow pits, JARE ice cores, and ITASE cores, respectively. The blue line between Syowa and DF denotes the JARE traverse along which surface accumulation has been measured. Abbreviations are listed in Table 1.

Table 1
Location, period, accumulation rate, and temporal resolution of ice cores and snow pit sites. Accumulation rates and time resolutions are averaged from the surface to 1966 (or bottom).

Site	Longitude	Latitude	Elevation (m a.s.l.)	Year of sampling	Period covered	Accumulation rate (kg m^{-2} a^{-1})	Time resolution (years)
DF	39°47′E	77°18′S	3785	2007	1966–2006	27.3 ± 16.8	0.25
DK	31°45′E	76°48′S	3733	2007	1986–2006	34.8 ± 13.4	0.21
MP	25°50′E	75°53′S	3656	2007	1971–2006	40.7 ± 13.1	0.18
YM85	40°38′E	71°35′S	2246	2002	1966–1998	128.2 ± 57.3	0.16
H72	41°05′E	69°12′S	1214	1998	1966–1997	305.7 ± 98.7	0.10
ITASE00-1	112°46′W	80°37′S	1791	2000	1966–2000	236.0 ± 62.1	0.06
ITASE00-4	121°55′W	79°55′S	1697	2000	1966–1999	184.5 ± 40.9	0.08
ITASE01-2	103°05′W	78°09′S	1336	2001	1966–2001	466.6 ± 77.0	0.06
ITASE01-5	90°52′W	78°56′S	1140	2001	1966–2000	346.9 ± 86.0	0.03
ITASE02-4	108°01′W	87°30′S	2586	2002	1966–1997	117.9 ± 38.2	0.09

millennial scales (e.g., Dansgaard, 1964; Fujita and Abe, 2006; Fernandoy et al., 2012). We therefore calculate the correlation coefficients for major ions and $\delta^{18}O$, and then compare these correlations with the accumulation rate and other parameters such as distance from coast, elevation, and latitude.

3. Results

3.1. Stable oxygen isotope and major ion signals

Accumulation rates along the JARE traverse gradually decrease with increasing latitude (Fig. 2a). We also find high variability in accumulation rates at lower latitudes (error bars in Fig. 2a). We therefore define a katabatic region using a coefficient of variation (CV) threshold of 1 (averaged every 1° of latitude) (Fig. 2b), as

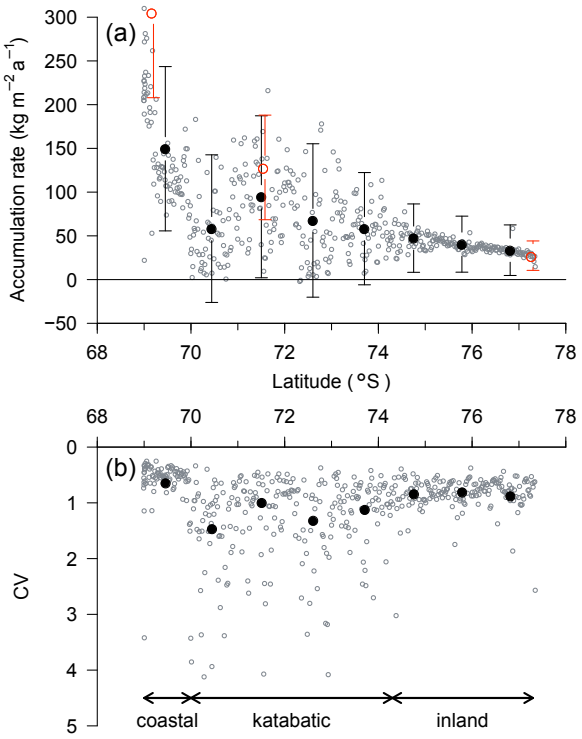

Fig. 2. (a) Average accumulation rate, and (b) coefficient of variation (CV) along the JARE traverse route for the period 1993–2010. Open gray and solid black circles denote the values of the individual stakes placed at 2-km intervals and those averaged at 1° of latitude, respectively. Open red circles denote the accumulation rates at H72, YM85, and DF. Error bars are standard deviations (1σ). The regions are identified based on the CV (see Section 3.1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

frequent wind erosion and thus loss of annual snow is expected to be associated with a high CV. We then categorize the traverse route into three regions: coastal (69.0°S–69.7°S), katabatic (69.7°S–74.3°S), and inland (74.3°S–77.3°S).

The JARE ice core sites are located in the coastal (H72) and katabatic (YM85) regions, whilst the JASE pit sites are situated in the inland region. Large variability in the accumulation rate in the katabatic region is reflected in both the CVs of individual stake measurements (>2 of CV) and in average values at 1° latitude intervals (>1 of CV) (Fig. 2b). Negative accumulation rates, usually caused by wind erosion, are commonly observed in this region (Furukawa et al., 1996), and it is therefore expected that the seasonal cycle of chemical components and water stable isotopes would not be preserved in the YM85 core.

Figs. 3 and 4 show Na^+, $CH_3SO_3^-$, and $nssSO_4^{2-}$ profiles along with $\delta^{18}O$ from ice cores and snow pits, ordered from high (top) to low (bottom) accumulation rates. Cl^- profiles are not shown because of strong correlations with Na^+ ($r > 0.84$) at all sites. $\delta^{18}O$ and major ion signals have high-frequency variability at sites with high accumulation rates (upper sites in Figs. 3 and 4) and become smoother at sites with low accumulation rates (lower sites in Figs. 3 and 4). At the high-accumulation sites, $nssSO_4^{2-}$ peaks seem to correspond with those of $\delta^{18}O$ (Fig. 4a–e); however, this relationship is less clear at the lower-accumulation sites (Fig. 4f–j). Furthermore, $CH_3SO_3^-$ is clearly in-phase with $nssSO_4^{2-}$ at two sites (DK and DF) during periods of low accumulation (Fig. 4i and j).

Periodicities of chemical signals in snow packs and ice cores were calculated using the Fast Fourier Transformation (FFT) to evaluate the preservation of original chemical seasonal cycles. The time interval of the samples is not uniform, so the periodicity was calculated using interpolated data. The trend found in Fig. 4, in which the signal frequency becomes unclear at low accumulation rates, is also found in statistically significant major ion and $\delta^{18}O$ FFT periods plotted against the accumulation rate (Fig. 5). At sites where the accumulation rate is >100 kg m^{-2} a^{-1}, $\delta^{18}O$, $nssSO_4^{2-}$, and $CH_3SO_3^-$ profiles show multi-year fluctuations, but at low-accumulation sites they show no annual cycle (Fig. 5a, c, and d). The Na^+ profile, however, exhibits both multi-year and annual cycles at low-accumulation sites (Fig. 5b). $CH_3SO_3^-$ and $nssSO_4^{2-}$ exhibit similar trends at low and high accumulation sites (Fig. 5c and d).

3.2. Correlations between major ions and stable oxygen isotopes

As chemical components in ice cores and snow pits have different temporal resolutions and frequencies (Table 1 and Fig. 5), we compare annual variations in ions and $\delta^{18}O$ after removal of the seasonal cycle to investigate the influence of the accumulation rate on the preservation of major ion signals. Although ion concentrations over Antarctica are controlled by various factors such as

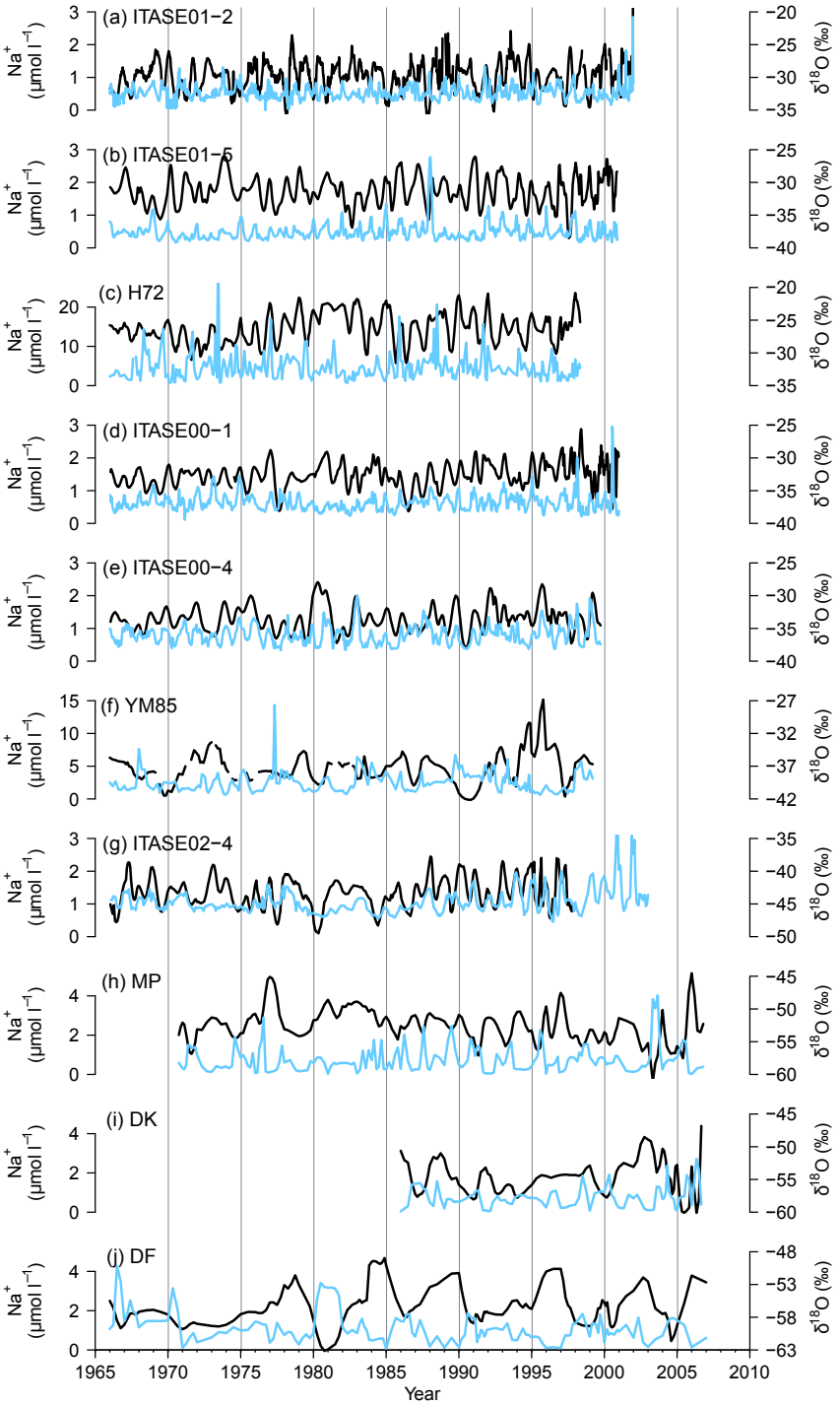

Fig. 3. Profiles of Na^+ (blue) and $\delta^{18}O$ (black) in ice cores and snow pits ordered from high (top) to low (bottom) accumulation rates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

distance from the source to the sampling site, precipitation seasonality, and the contribution of dry and wet deposition, it is not possible to reconstruct the spatial distribution of these factors from post-depositional snow samples. On the other hand, annual temperature, which is generally recorded in water stable isotopes, is a key variable to help understand the distribution of other chemical species in snow and ice profiles. We therefore calculate correlation coefficients between major ions and as it implies that the correlation is based on $\delta^{18}O$ as a temperature proxy (Dansgaard, 1964; Fujita and Abe, 2006; Fernandoy et al., 2012).

Fig. 6 shows the correlation coefficients for annually averaged concentrations and fluxes of major ions and $\delta^{18}O$ plotted against the accumulation rate. There are no significant differences between concentrations (Fig. 6a) and fluxes (Fig. 6b). It is expected that the correlations of Cl^- and Na^+ with $\delta^{18}O$ would have similar signals due to their common origin from the ocean. However, they show no correlation when the accumulation rate is >185 kg m^{-2} a^{-1}. Additionally, correlations become gradually more negative from coastal

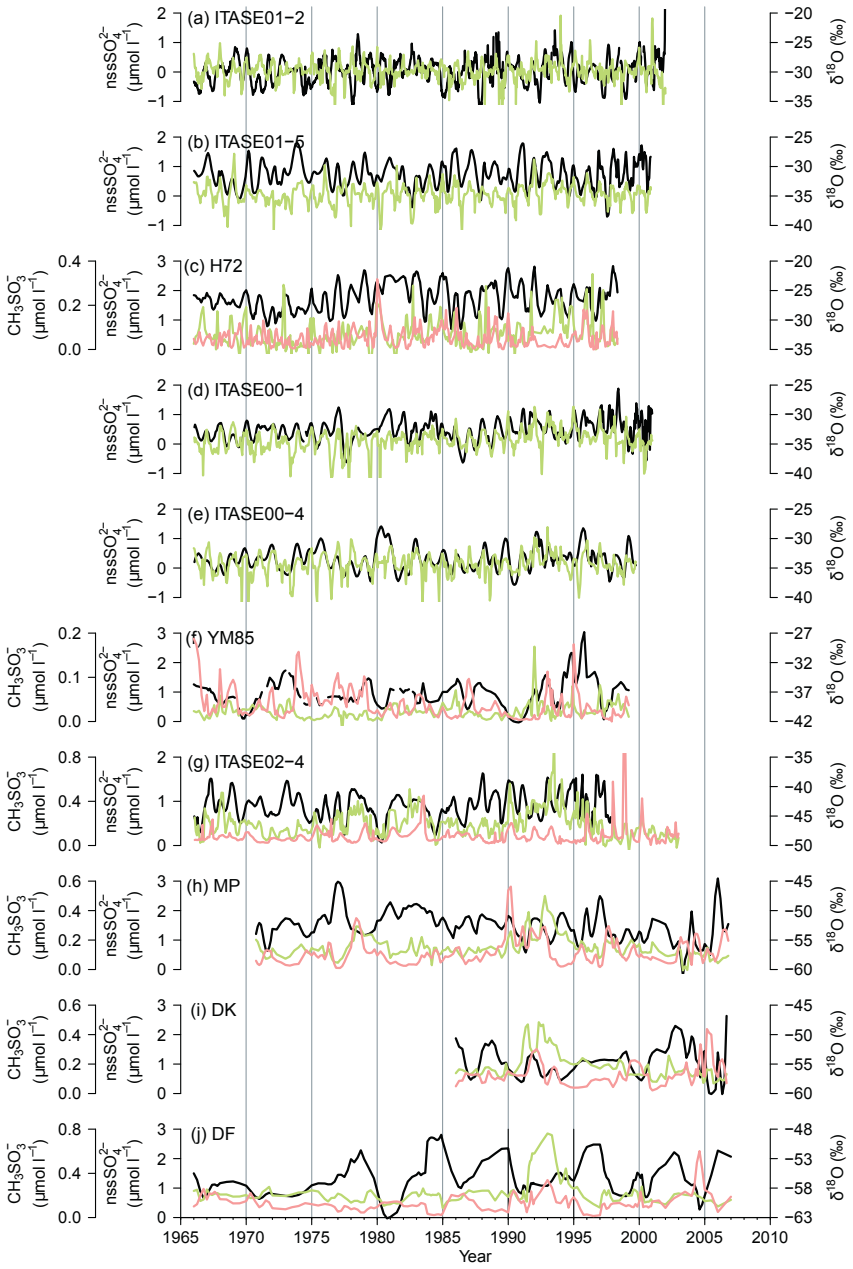

Fig. 4. Profiles of $CH_3SO_3^-$ (pink), $nssSO_4^{2-}$ (green), and $\delta^{18}O$ (black) in ice cores and snow pits ordered from high (top) to low (bottom) accumulation rates.

high-accumulation regions to the inland low-accumulation regions, where significant negative correlations were found. Temporal series of Na^+ and $\delta^{18}O$ also show that minimum Na^+ and maximum $\delta^{18}O$ values are most consistent at the lowest-accumulation sites (MP, DK, and DF in Fig. 3h–j). On the other hand, $CH_3SO_3^-$ and $nssSO_4^{2-}$ have insignificant (slightly positive) correlations with $\delta^{18}O$ at both high and low accumulation regions, but correlations become significant at the lowest-accumulation sites. NO_3^- is positively correlated with $\delta^{18}O$ for accumulation rates of 100–200 kg m^{-2} a^{-1}, but no significant correlation is found for accumulation rates of >200 kg m^{-2} a^{-1} and <100 kg m^{-2} a^{-1}.

4. Discussion

4.1. Spatial variability in accumulation rates

The seasonal cycle of oxygen isotopes and major ions in ice cores and snow pits is preserved at sites with accumulation rates >100 kg m^{-2} a^{-1} (Fig. 5) despite the fact that snow at individual sites has different sources and transport pathways. Moreover, relationships between isotopes, major ions, accumulation rates, and geographical variables differ for ice core sites in East and West Antarctica. Fig. 7 shows correlation coefficients for both major ions and $\delta^{18}O$ with elevation, latitude, distance from the coast, and 10-m snow temperature. Trends in correlation coefficients with elevation (Fig. 7a) and 10-m temperature (Fig. 7d) are related to the strong negative correlation between elevation and both annual

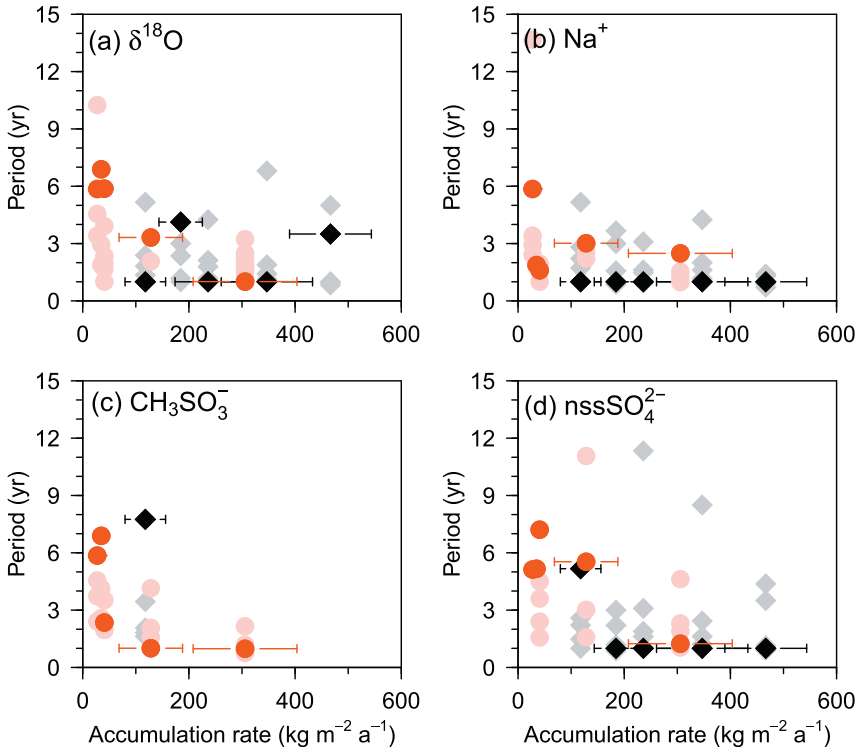

Fig. 5. Results of FFT analyses showing significant power intensities of (a) $\delta^{18}O$, (b) Na^+, (c) $CH_3SO_3^-$, and (d) $nssSO_4^{2-}$ profiles in East (red and pink circles) and West (black and gray diamonds) Antarctica. Red and black denote the highest power intensity, and gray and pink denote statistically significant intensity. Error bars are standard deviations (1σ).

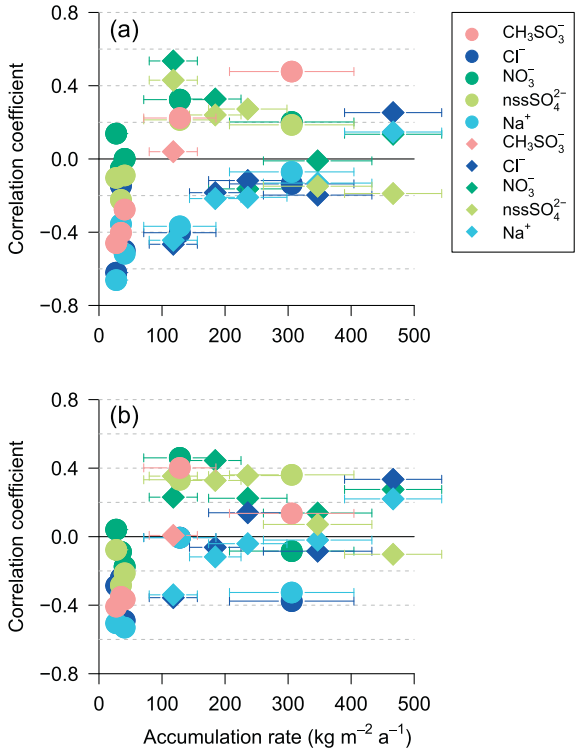

Fig. 6. Correlation coefficients between major ions and $\delta^{18}O$ plotted against accumulation rate in terms of annual (a) correlation, and (b) flux in East (circles) and West (diamonds) Antarctica.

temperature (higher elevations result in colder temperatures) and accumulation rates (Fig. 6). The 10-m temperature trend is explained by the Clausius–Clapeyron equation in which colder temperatures result in drier air masses. On the other hand, latitude (Fig. 7b) and distance from the coast (Fig. 7c) do not completely depend on the correlation coefficients. This discrepancy is explained by the correlations between geographical variables and the accumulation rate; the accumulation rate has a strong correlation with elevation ($r = -0.80$, $p < 0.05$) and 10-m temperature ($r = 0.86$, $p < 0.05$), but this is not the case for latitude ($r = -0.02$, $p = 0.96$) or distance from the coast ($r = -0.70$, $p < 0.1$).

Suzuki et al. (2013) used back trajectory analysis to show that air parcels over West Antarctica mainly originate from the ocean year-round, whereas source regions for air parcels over East Antarctica are seasonal, originating from inland in summer and from the ocean in winter. Sodemann and Stohl (2009) also indicated a difference in moisture sources for coastal and inland Antarctica. The insignificant relationship between latitude and distance from the coast (Fig. 7) most likely reflects the different transportation processes of air parcels over East and West Antarctica. The strong correlations between elevation, 10-m temperature, and accumulation rate suggest that the accumulation rate is governed by elevation and to a lesser extent temperature. Similarity in the spatial distribution of precipitation with elevation (Bromwich et al., 2004) also supports the relationship suggested above. Correlation coefficients for the above-mentioned geographical variables assume average conditions over Antarctica, while those between the major ions and $\delta^{18}O$ (Figs. 6 and 7) reflect the inter-annual variability of major ions and temperature.

Our classification of the JARE traverse route (coastal, katabatic, and inland regions) based on the CV of the accumulation rate (Fig. 2) is broadly consistent with that used by Furukawa et al. (1996). These authors identified uniform accumulation zones by

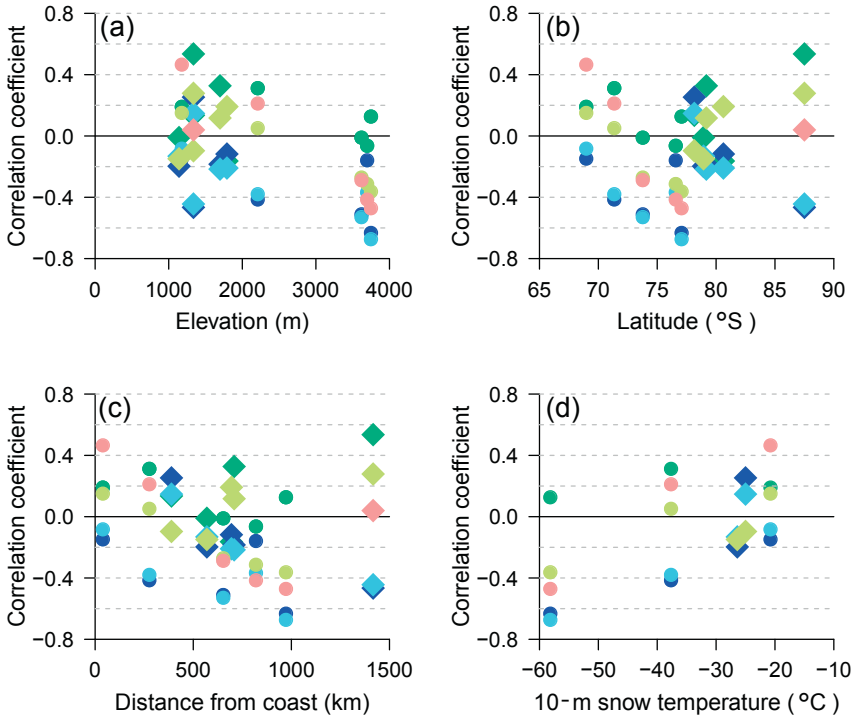

Fig. 7. Correlation coefficients between major ions and $\delta^{18}O$ for (a) elevation, (b) latitude, (c) distance from the coast (Table 2), and (d) 10-m snow temperature (Table 2) in East (circles) and West (rhombuses) Antarctica. Symbol colors indicate $CH_3SO_3^-$ (pink), Cl^- (blue), NO_3^- (green), SO_4^{2-} (light green) and Na^+ (light blue).

Table 2
Distance from the coast and 10-m snow temperature of ice cores and snow pits used in this study.

Site	Distance from coast (km)	10-m Snow temperature (°C)
DF	986	−57.7 (Kameda et al., 2007)
DK	833	
MP	667	
YM85	290	−37.2 (Satow and Watanabe, 1992)
H72	53	−20.3 (Nishio et al., 2002)
ITASE00-1	475[a]	
ITASE00-4	460[a]	
ITASE01-2	295[a]	−25.0 (Dixon, 2007)
ITASE01-5	400[a]	−26.4 (Dixon, 2007)
ITASE02-4	1074	

[a] Dixon et al. (2004).

analyzing offshore cyclones in the high-accumulation coastal region, sporadic accumulation zones in the katabatic region, and low-accumulation inland zones, based on surface features observed during multiple expeditions between October 1992 and January 1994. According to these categories, the YM85 core is located in the katabatic region, and Takahashi et al. (2009) concluded that the high accumulation rate should result in the preservation of annual layers and seasonal cycles in the core. Our analysis suggests that seasonal cycles are not preserved in the YM85 core (Figs. 3f, 4f and 5), but seasonal cycles are preserved in the ITASE02-4 core (Figs. 3g, 4g and 5), although the accumulation rate of the ITASE02-4 core (118 kg m^{-2} a^{-1}; Mayewski and Dixon, 2013) is estimated to be less than that of the YM85 core (128 kg m^{-2} a^{-1}). In addition, seasonal cycles are also preserved in the ITASE00-1 core (Figs. 3d, 4d and 5), although the site appears to be characterized by strong winds, with monthly average winter wind speeds at a nearby automatic weather station of >10 m s^{-1} (Keller et al., 2003, 2007, 2008).

Stake measurements taken along the JARE traverse route show that the annual accumulation rate is often negative in the katabatic region as a result of surface erosion (Fig. 2a). These measurements also suggest that sites with accumulation rates of >200 kg m^{-2} a^{-1} are less susceptible to surface erosion. We therefore conclude that seasonal cycles in the YM85 core were disturbed by katabatic wind because of insufficient accumulation rates (<200 kg m^{-2} a^{-1}), while the two ITASE sites result in preservation of seasonal cycles under low accumulation in the calm region (ITASE02-4) or high accumulation in the katabatic region (ITASE00-1).

4.2. Negative correlations between major ions and $\delta^{18}O$ at low-accumulation sites

Correlation coefficients between major ions and $\delta^{18}O$ in ice cores and snow pits across East and West Antarctica show slightly positive ($CH_3SO_3^-$ and $nssSO_4^{2-}$) or no (Na^+ and Cl^-) correlation at sites with high accumulation rates (>150 kg m^{-2} a^{-1}), whereas strong negative correlations are found for the majority of ions (except for NO_3^-) at sites with low accumulation rates (<100 kg m^{-2} a^{-1}) (Fig. 6). Similarly, negative correlations between ions and $\delta^{18}O$ are found in ice cores from west Dronning Maud Land. Isaksson et al. (2001) did not indicate any significant correlations between major ion concentrations and $\delta^{18}O$, but show negative correlations in 7-year moving variations of major ions concentrations and $\delta^{18}O$ in the Amundsenisen ice core, where the annual accumulation rate was estimated to be 70–80 kg m^{-2} a^{-1} (Isaksson et al., 1996). On the other hand, negative correlations are not found in ice cores at high-accumulation sites such as Styx Glacier (203 kg m^{-2} a^{-1}) and McCarthy Ridge (260 kg m^{-2} a^{-1}) (Stenni et al., 2000). Given that sources and transportation processes might be different between sampling sites (Suzuki et al., 2013), our data (Fig. 6) and other records suggest that the relationship between the major ions and $\delta^{18}O$ is governed by the accumulation rate, which reflects both elevation and the annual

average temperature (Fig. 7a and d). In particular, negative correlations between major ions and $\delta^{18}O$ are most common at low-accumulation sites (<100 kg m^{-2} a^{-1}).

Considering that seasonal cycles are preserved in ice cores from humid environments (Figs. 3–5), the original relationship between $\delta^{18}O$ and the major ions should not be statistically significant on an inter-annual timescale (Fig. 6). In extremely low-accumulation environments, on the other hand, Hoshina et al. (2014) found that multi-year cycles of $\delta^{18}O$ in JASE snow pits (MP, DK, and DF) are not correlated with air temperature fluctuations. They speculated that the multi-year cycle could result from post-depositional alterations, such as ventilation (airflow from the surface through the firn layer) and/or the condensation–sublimation of vapor driven by non-uniform accumulation (Kameda et al., 2008). Ventilation may also smooth the $\delta^{18}O$ trough in winter, and this effect may be more pronounced in low-accumulation environments (Neumann and Waddington, 2004; Town et al., 2008).

Town et al. (2008) considered diffusion processes solely for oxygen isotopes; however, we suggest that vapor transfer processes between the snow pack and atmosphere could also modify major ions and hence form negative correlations with $\delta^{18}O$. When water vapor sublimates from ice grains under extremely low temperatures, isotopic fractionation does not occur because of the slow divergence of water molecules within ice grains, but ion concentrations increase due to sublimation processes. On the other hand, the condensation of water vapor should cause isotopic fractionation and increase $\delta^{18}O$ and dilution should decrease ion concentrations. In particular, condensation of water vapor from the atmosphere to near-surface snow will modify $\delta^{18}O$ and ion concentration of snow by ventilation (Town et al., 2008) and/or form surface hoar. Such changes in $\delta^{18}O$ and ion concentrations could potentially modify their original relationships, and negative correlations would be enhanced by low accumulation and high variability in accumulation rates (Hoshina et al., 2014).

In low-accumulation environments, the negative relationship between Na^+ and $\delta^{18}O$ in snow shows seasonal fluctuations (Iizuka et al., 2004). Na^+ in the snow pack in low-accumulation environments shows both annual and multi-year fluctuations (Fig. 5b); however, $\delta^{18}O$ shows only multi-year cycles formed by post-depositional alterations such as ventilation and/or condensation–sublimation of vapor (Hoshina et al., 2014). The negative relationship between Na^+ and $\delta^{18}O$ at a seasonal scale is lost between snow precipitation and the snow pack, and the negative relationship in multi-year fluctuations is enhanced. Similar relationships between Na^+ and $\delta^{18}O$ have been proposed from recent ice core evidence (Wolff et al., 2006; Röthlisberger and Abram, 2009). Our results indicate that Na^+ is most effective on a multi-year scale as an ice-core proxy for past temperature, even if annual scale fluctuations are preserved.

It is still unclear, however, why the relationships between Na^+ and Cl^- and $CH_3SO_3^-$ and $nssSO_4^{2-}$ vary with the accumulation rate (as shown by correlation coefficients with $\delta^{18}O$ in Fig. 6). The trends towards more negative Na^+ and Cl^- correlations with lower accumulation rates suggest that negative relationships were formed during transportation. However, the relationship between $CH_3SO_3^-$ and $nssSO_4^{2-}$ seems to be insignificant throughout Antarctica except at very low accumulation sites (Fig. 6). To clarify these findings we need more evidence from the various environments across Antarctica to better understand paleo-environmental proxies and chemical signals embedded in snow and ice cores.

5. Conclusions

We compare major ions with $\delta^{18}O$ in shallow ice cores and snow pits under different accumulation environments in East and West Antarctica. Despite different sources and transportation processes, correlation coefficients among annually averaged components show similar trends; i.e., correlations of Na^+ and Cl^- with $\delta^{18}O$ gradually change from showing no correlation to exhibiting negative correlations with decreasing accumulation, while those of $CH_3SO_3^-$ and $nssSO_4^{2-}$ are only significantly negative in the most arid environments in inland Antarctica (Fig. 6). Our analyses, using data from sites with a range of accumulation rates, indicate that an accumulation rate of 100 kg m^{-2} a^{-1} is the threshold for formation of a negative correlation between chemical species. In addition, the original seasonal cycle can be preserved in snow if the accumulation rate is greater than the threshold under calm wind conditions, whereas the cycle is unclear in the katabatic region, even if the accumulation rate is greater than the threshold.

Significant negative correlations in very low-accumulation environments can be formed by ventilation and vapor transfer within snow and the formation of surface hoar, which potentially increases $\delta^{18}O$ by isotopic fractionation and dilutes ion concentrations. Recent advances in analytical technologies allow ice-core researchers to deal with fine temporal resolutions, such as decadal to annual time scales (Steig et al., 2005; Iizuka et al., 2006; de Angelis et al., 2013). However, Hoshina et al. (2014) demonstrated that periodic signals embedded in snow under extremely arid environments were multi-year and not seasonal. They concluded that these multi-year cycles could be formed by post-depositional alteration, driven by the variable accumulation of snow due to low accumulation rates with large inter-annual variability.

This study demonstrates that relationships between major ions and $\delta^{18}O$ may not reflect the climatic footprint, but may be a unique signal of major ions and $\delta^{18}O$ in extremely arid environments. We also show that the accumulation rate (with a threshold of 100 kg m^{-2} a^{-1}) and wind speed affect the preservation of seasonal cycles in snow. Recent accumulation events over East Antarctica might form major ion and $\delta^{18}O$ seasonal cycles if annual accumulation exceeds the threshold. Our analysis also shows that elevation and annual mean temperature correlate well with accumulation rates. This finding suggests that climate change associated with glacial to inter-glacial cycles might significantly alter the accumulation rate and thus form different periodicities in the respective climates.

To better understand processes that govern the formation of negative correlations between chemical species in snow and ice records, more evidence is required from very arid environments, such as those favored for drilling deep ice cores. In addition, we speculate that processes such as ventilation and vapor transfer within snow and the formation of surface hoar could alter $\delta^{18}O$ and major ion concentrations in post-depositional environments. In situ observational and/or experimental research will help to quantitatively evaluate the contributions of these processes.

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