An emerging technique: multi-ice-core multi-parameter correlations with Antarctic sea-ice extent

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ABSTRACT. Using results stemming from the International Trans-Antarctic Scientific Expedition (ITASE) ice-core array plus data from ice cores from the South Pole and Siple Dome we investigate the use of sodium (Na^+), non-sea-salt sulfate ($nssSO_4^{2-}$) and methylsulfonate (MS^-) as proxies for Antarctic sea-ice extent (SIE). Maximum and mean annual chemistry concentrations for these three species correlate significantly with maximum, mean and minimum annual SIE, offering more information and clarification than single ice-core and single species approaches. Significant correlations greater than 90% exist between Na+ and maximum SIE; $nssSO_4^{2-}$ with minimum and mean SIE; and MS^- with mean SIE. Correlations with SIE within large geographic regions are in the same direction for all ice-core sites for Na^+ and $nssSO_4^{2-}$ but not MS^-. All ice cores display an SIE correlation with $nssSO_4^{2-}$ and MS^-, but not all correlate with Na^+. This multi-core multi-parameter study provides the initial step in determining which chemical species can be used reliably and in which regions as a building block for embedding other ice-core records. Once established, the resulting temporal and spatial matrix can be used to relate ice extents, atmospheric patterns, biological productivity and site conditions.

INTRODUCTION

Recent observations demonstrate that Arctic sea ice is decreasing (Parkinson and Cavalieri, 2008), particularly in summer and early autumn (ACIA, 2004). Overall Antarctic sea ice is increasing on a much smaller scale than Arctic decreases, although this increase includes individual regions in which sea ice is decreasing (Cavalieri and Parkinson, 2008; Turner and others, 2009a).

Knowledge of changes in past and prediction of future Antarctic sea-ice extent (SIE) is imperative. The annual growth and retreat of Antarctic sea ice imparts changes on both regional and global scales and on short and long timescales. Changes in sea ice affect deep ocean water formation and circulation (Stössel and others, 2002), albedo (Curry and others, 1995), primary production and phytoplankton blooms (Arrigo and Van Dijken, 2004) and global climate variability through association with El Niño Southern Oscillation (ENSO), sea surface temperature (SST) and global surface temperature (Yuan and Martinson, 2000).

Conversely, atmospheric circulation patterns influence sea-ice variability directly. Simmonds and Jacka (1995) found a correlation between SIE and the Southern Oscillation Index (SOI). SOI, an index based on sea-level pressures (SLPs) measured at Tahiti and Darwin, is correlated to SIE in the southwestern Indian Ocean (35–65° E), southwestern Pacific Ocean (155–175° E), southeastern Pacific Ocean (225–255° E) and west of the Ross Sea (125–165° E). Carleton (1989) examined SIE changes and the large-scale atmospheric circulation patterns of the SOI and SLP in the Ross and Weddell Seas. Based on the 10 year dataset used in that study, SIE changes lagged the SOI but led SLP changes. Linkages between SOI and SIE anomalies were found using a 17 year dataset covering the period 1982–98 (Kwok and Comiso, 2002). The strongest connections found in this study were in the Ross–Amundsen Seas and the Bellingshausen–Weddell Seas, although the correlations between these regions were opposite in sign. ENSO and the Antarctic Oscillation (AAO), a representation of the strength of the

polar vortex, were found to be related to SIE changes (Liu and others, 2004) such that positive phases of the AAO led to more ice in the Ross–Amundsen sector but less ice in the Bellingshausen–Weddell sector. Turner and others (2009b) found a positive trend in SIE in the Ross Sea related to stronger cyclonic circulation associated with changes in the thermal gradient induced by stratospheric ozone depletion.

Sea ice is commonly quantified by determining extent away from the continent (SIE), length of time present (duration), concentration, or amount of open water. All approaches are more accurate and extensive since the implementation of routine satellite observations in 1978. Prior to 1978, extent and concentration data are based on shipboard observations, whaling records, marine sediment cores, ice-core proxies and sporadic satellite remote sensing (1973–78). Published snow and ice-core sea-ice proxy data are fairly limited, and, with a few exceptions, results are generally based on the use of one chemical species measured on samples collected from a single ice-core site.

The primary chemical species used for sea-ice reconstruction are sodium, non-sea-salt sulfate and methanesulfonic acid, all of which are routinely measured using ion chromatography (Legrand and Mayewski, 1997). Sodium in Antarctic ice is almost exclusively representative of sea-salt inputs and is preserved and measured in ice cores as Na^+. Sulfate is also supplied from sea salts but the larger contribution is from non-marine sources such as atmospheric transport of volcanic and biogenic sulfate, crustal emissions and, in Antarctica, a small amount of anthropogenic inputs from industrial emissions and agricultural processes. Non-sea-salt sulfate ($nssSO_4^{2-}$) is commonly calculated using Na^+ as a conservative tracer in the ocean (Pilson, 1998). Methanesulfonic acid (MSA) has only one source in Antarctica, notably marine phytoplankton processes and subsequent oxidation of resultant dimethylsulfide (DMS) in the atmosphere. Specific processes that produce DMS include degassing from melting sea ice (Gabric and others, 2005; Trevena and Jones, 2006; Jones and others,

2009) and phytoplankton blooms (DiTullio and others, 2000). MSA is preserved and measured in ice cores as methylsulfonate (MS^-).

Previous work on SIE–chemistry correlations typically has been based on single snow pits or ice cores and a single chemical species. Antarctic sites investigated include coastal (Welch and others, 1993; Curran and others, 2003; Rhodes and others, 2009), near-coastal (Sun and others, 2002; Foster and others, 2006) and inland (Petit and others, 1999; Meyerson and others, 2002; Wolff and others, 2006). Alternatively, a few studies used more varied approaches to develop sea-ice proxies. Pasteur and others (1995) used the biogenic sulfur compounds $nssSO_4^{2-}$ and MS^- on a single coastal core. These two species were also measured on a coastal snow pit (Severi and others, 2009). A record using two different types of core (the Dome C (Antarctica) ice core and an Indian Ocean sector marine core) and two different proxies (chemistry and diatom assemblages, respectively) yielded an SIE record for the Indian Ocean region (Röthlisberger and others, 2010). Another alternative to single-core–single-species proxy development combined chemistry data for one proxy measured on multiple cores to determine regional sea-ice correlations (Abram and others, 2007). Kaspari and others (2005) compared one species to SIE on a suite of 16 ice cores. Dixon and others (2005) were the first to examine SIE correlations using two chemical species on multiple ice cores. Some details of the previous studies follow.

SODIUM

Na^+ is delivered to Antarctica primarily in winter/spring although the exact source of the sea salt is debated. There are two primary contenders.

1. Increased wind speed and strength in winter/spring of features such as the Amundsen Sea low enhance sea-salt aerosol transport to Antarctica (Kreutz and others, 2000; Kaspari and others, 2005). Sea-salt concentrations in the Siple Dome ice core are associated with changes in surface pressure ($r = 0.32$, >95% confidence) in the region of the Amundsen Sea low (Kreutz and others, 2000). Additionally, changes in cyclonic activity correlate with accumulation rates in the Pine Island–Thwaites drainage region, West Antarctica (Kaspari and others, 2004). Ice-core accumulation rates correlate ($r = 0.345$) with changes in surface pressure. Strong surface pressure and Na associations exist throughout a large portion of West Antarctica. Kaspari and others (2005) determined positive correlations between Na measured in central West Antarctic ice-core sites and specific marine regions. Two ice cores correlated with the SIE ($r = 0.35$) in the Bellingshausen and east Amundsen Seas and a third site correlated with SIE in the west Amundsen and Ross Seas region ($r > 0.35$).

2. Formation of new sea ice in winter yields increased Na^+ concentrations (Rankin and others, 2002). The latter association is based on the presence of frost flowers: fragile, briny crystals that form on new sea-ice surface. These crystals preferentially precipitate sodium sulfate (as mirabilite, $Na_2SO_4 \cdot 10H_2O$), resulting in aerosols depleted in SO_4^{2-}. Both processes result in a positive correlation between Na^+ and SIE, but may be distinguished by the Na^+ to SO_4^+ ratio.

To investigate the frost flower as an Na^+ source, Rankin and others (2002) analyzed data from an ice core collected from Dolleman Island on the east coast of the Antarctic Peninsula. The Na^+ to SO_4^+ ratio indicated that most of the Na^+ was found in the fractionated, or winter, portion of the year.

Na^+ has been invoked as a proxy for sea ice in several deep ice-core studies. Wolff and others (2003) suggested that increased sea-ice production was the source of Na^+ to the Antarctic plateau. Applying this to the most recent 45 000 years of the much longer Dome C ice-core record yielded an association with SIE in the Indian Ocean sector (Wolff and others, 2006). As a possible test, Sun and others (2002) measured Na^+ from a core collected north of the Lambert Glacier basin, East Antarctica. That site has no correlation with annual SIE in either the Indian Ocean region or with the annual mean sea-ice area around the entire continent over the 60 year record of the core.

Recently, a longer section of the Dome C record was compared with a marine sediment core (Röthlisberger and others, 2010). The marine core was collected in the Indian Ocean sector and the records compared over the past 240 000 years. Diatom assemblages in the marine core were related to seasonal changes in sea ice during full glacial conditions, and the ice-core Na^+ was related to sea-ice changes during the interglacial and early glacial periods. In both Dome C investigations the associations are qualitative since Dome C Na^+ and SIE were not calibrated using modern Na^+ and satellite-based SIE records.

A positive correlation is found in the Vostok (East Antarctica) core (Petit and others, 1999) between Na^+ and sea-ice volume. Sea-ice volume in this 420 000 year long record was reconstructed using sea-water $\delta^{18}O$. Polar ice is depleted in $\delta^{18}O$ as a consequence of fractionation during transport. During glacial periods, increased ice (both glacial and sea ice) drive sea-water $\delta^{18}O$ higher. Thus, determination of the $\delta^{18}O$ time series from marine biogenic material leads to a proxy for ice volume. A positive association (increased Na^+ with increased ice volume) is suggested from this study for the four glacial periods represented.

NSS-SULFATE

The dominant source of $nssSO_4^{2-}$ is the oxidation of DMS produced by marine phytoplankton in summer (Minikin and others, 1998). This process supplies ~40% of the $nssSO_4^{2-}$ to the Southern Hemisphere (Gondwe and others, 2003). Other sources include non-DMS biological activity, distant anthropogenic processes and infrequent volcanic eruptions. In Antarctica, volcanic events are identifiable by a relatively large increase in background concentrations of sulfate.

A core collected from Dolleman Island showed an anticorrelation at the 95% confidence level ($r = -0.29$, $n = 88$) between $nssSO_4^{2-}$ and sea-ice duration in the Weddell Sea (Pasteur and others, 1995). This work suggests that for the period 1900–92 increased (decreased) sea-ice duration was correlated with decreased (increased) $nssSO_4^{2-}$ concentration. The 200 year record of Dixon and others (2005) also suggested increased $nssSO_4^{2-}$ with decreased SIE at several sites in West Antarctica ($r \geq 0.414$–0.514, $18 \leq n \leq 24$, >95% confidence). In Dixon and others' (2005) study, the Weddell Sea exhibits the greatest number of correlations (18) with the greatest number of ice-core sites (10). However, as with Kaspari and others (2005), this multi-chemistry multi-core approach revealed more complex associations between

Table 1. Site information of ice cores used in this study

Core	Latitude	Longitude	Elevation m a.s.l.	Time period	Accumulation g cm^{-2} a^{-1}	Sampling resolution cm	Source
Siple Dome	81.648° S	148.790° W	620	1994–1979	11.88	2–10	Mayewski and others (1995)
01-4	77.612° S	92.248° W	1483	2000–1979	32.5	2.0–3.3	This study
02-1	82.001° S	110.008° W	1746	2000–1979	19	4	This study
02-4	86.503° S	107.990° W	2586	2002–1979	11	1.80–4.14	D. Dixon and others (unpublished information)
South Pole	90.000° S	0.000°	2850	2000–1979	7.34	2	Meyerson and others (2002), Budner and Cole-Dai (2003)
03-1	86.840° S	95.310° E	3124	2003–1979	4.6	1.4–2.9	D. Dixon and others (unpublished information)

chemistry, core site and SIE region. Factors affecting transport and deposition of chemical species include site elevation and distance from the source, atmospheric circulation changes and conditions at the source.

METHYLSULFONATE

MS$^-$ is the species used most extensively as a proxy for sea ice. The only source of MS$^-$ to the atmosphere is the oxidation of DMS, and DMS is produced by phytoplankton (Saigne and Legrand, 1987). Although the exact branching ratio of MS from DMS is not well understood, it is still a valuable indicator of marine productivity. Increased marine productivity associated with sea-ice retreat has been measured by remote sensing in areas of the Ross and Weddell Seas (Moore and Abbott, 2000).

Welch and others (1993) showed a positive correlation at the 99% confidence level between annual mean MS$^-$ and annual mean sea-ice area in both the Ross Sea region ($r = 0.802$, $n = 18$) and the entire Southern Ocean ($r = 0.768$, $n = 18$) using snow-pit samples from the coastal Newall Glacier covering the period 1971–90. Using a South Pole MS$^-$ ice-core record, Meyerson and others (2002) reported positive correlations ($r = 0.55$, $n = 20$) with SIE anomalies in the Amundsen–Ross Seas area. Less (more) MS$^-$ was noted to indicate less (more) sea ice in a core from Law Dome, East Antarctica, over the 22 years (1973–94) that overlapped the sea-ice record ($r = 0.48$, $p < 0.002$, $n = 22$) (Curran and others, 2003). A 10 m firn core from Wilhelm II Land, north of Law Dome (Foster and others, 2006), also yielded a positive correlation with SIE over the period 1984–98 for the region 60–120° ($r = 0.51$, $p < 0.05$, $n = 15$). Normalized and stacked MS$^-$ data from three cores collected from around the Weddell Sea region showed a positive correlation with maximum SIE ($r = 0.66$, $n = 18$, 95% confidence) in the Amundsen–Bellingshausen region, but a strong negative correlation ($r = -0.76$, 99% confidence) with Weddell Sea maximum SIE (Abram and others, 2007). Records used were Dolleman Island (Pasteur and others, 1995), Berkner Island (Mulvaney and others, 1992) and Dronning Maud Land covering the years 1973–90.

The Dolleman Island study by Pasteur and others (1995) utilized MS$^-$ as well as nssSO$_4^{2-}$ data and revealed an anticorrelation ($r = -0.23$, $n = 88$, 95% confidence) with sea-ice duration. An East Antarctic core from Lambert Glacier (Sun and others, 2002) also showed an anticorrelation between MS$^-$ and SIE in the Indian Ocean region ($r = -0.34$, $n = 25$, 95% confidence) for the period 1973–92. Recently,

Rhodes and others (2009) measured MS$^-$ in a snow pit (1999–2005) from Mount Erebus Saddle in the Ross Sea region and found a positive correlation with open-water extent ($r = 0.903$, $p < 0.5$, $n = 6$) inferred as a negative correlation with sea ice.

METHODS

During the 2008 International Trans-Antarctic Scientific Expedition (ITASE)/Scientific Committee on Antarctic Research (SCAR) workshop in Castine, ME, USA, it was decided that the ice-core community needed a more thorough examination of available data for sea-ice reconstructions. Here we present a starting platform to develop a matrix of multi-core multi-parameter SIE correlations to better understand patterns and trends, or lack thereof, in the preceding studies. The resulting matrix will provide spatial and temporal data to aid in the understanding of transport mechanisms, biological processes, influence of core site conditions and effects of sea-ice extents. We examine SIE correlations using the maximum and mean annual concentrations of three chemical species (Na$^+$, nssSO$_4^{2-}$ and MS$^-$) on a suite of Antarctic ice cores. We selected six ice cores of which two have not been reported previously (Fig. 1; Table 1). These cores are sampled continuously, well dated, resolved sub-annually (6–12 samples per year) and represent a wide range of geographic locations. Cores from West Antarctica (01-4, 02-1 and 02-4) and East Antarctica (03-1) were collected in 2001–02, 2002–03 and 2003–04 during the US ITASE field seasons. The South Pole record used here comes from Meyerson and others (2002) developed from a core collected in 1995. South Pole core data from 1979 to 1992 were stacked with results of another South Pole core collected in 2000 (Budner and Cole-Dai, 2003) to extend the record, and, in addition, were compared with another South Pole record (personal communication from E.~Korotkikh, 2010). The Siple Dome ice core was collected in 1994 (Mayewski and others, 1995).

An example of the dating technique used is presented in Figure 2. The majority of the cores used in this study were annually dated using seasonal peaks in major ions and calibrated to known volcanic eruptions (Dixon and others, 2004, 2005). The SO$_4^{2-}$ from the Pinatubo (Philippines) and Cerro Hudson (Chile) volcanic eruptions can be seen in the 02-4 glaciochemical time-series plot (Fig. 2). Both events occurred in 1991, causing the background concentration of SO$_4^{2-}$ to rise followed by a peak in SO$_4^{2-}$ in 1993. The 01-4, 02-1 and Siple Dome cores contain very clear seasonal
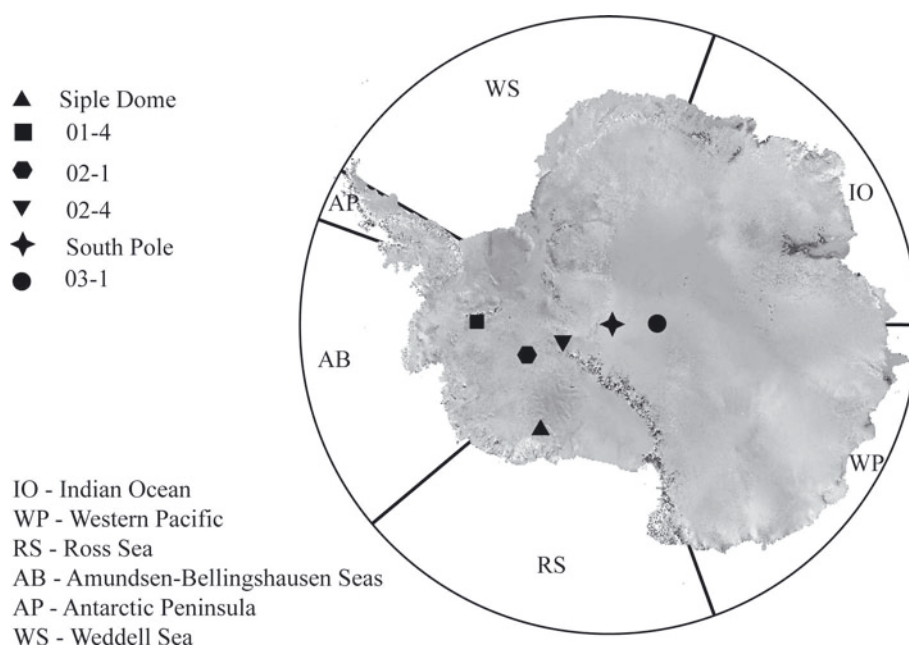
Fig. 1. Site map of ice cores used in this study. Longitudes of major SIE regions: IO, 20–90°; WP, 90–160°; RS, 160–230°; AB, 230–290°; AP, 290–300°; WS, 300–360°. Map created using Moderate resolution Imaging Spectroradiometer (MODIS) Mosaic of Antarctica (T. Haran and others, http://nsidc.org/data/nsidc-0280.html).
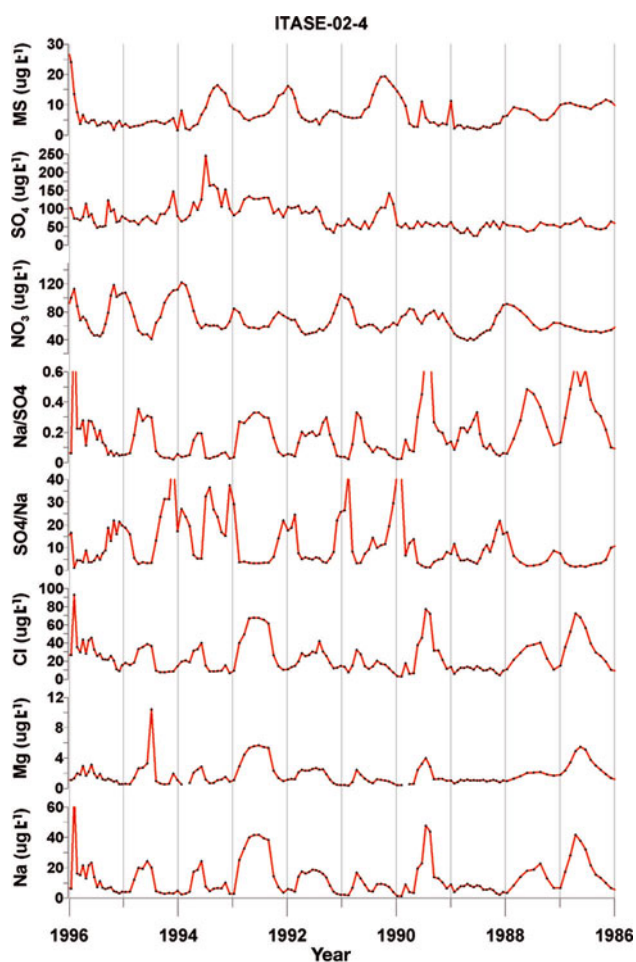

Fig. 2. Raw major-ion and MS data time series in core 02-4. Increase in background concentrations of sulfate following the 1991 Pinatubo and Hudson eruptions can be seen. Na/SO$_4$ ratios indicate winter, SO$_4$/Na peak in summer. H/D ratios (not shown) also used for dating (Steig and others, 2005).

SO$_4^{2-}$ peaks due to their proximity to the coast and their relatively high accumulation rates. The 02-4 and South Pole cores, being located further inland and with correspondingly lower accumulation rates, do not exhibit these clear annual SO$_4^{2-}$ peaks. However, clear annual layers can be distinguished at these two sites by examining Na$^+$/SO$_4^{2-}$ (winter) and SO$_4^{2-}$/Na$^+$ (summer) ratios. The 03-1 core was dated using volcanic depth/age horizons in combination with a firn compaction model.

Annual maximum and mean concentrations of Na$^+$, nssSO$_4^{2-}$ and MS$^-$ were calculated for each core and compared with SIE over the period 1979 (onset of continuous satellite SIE data) to the top of each core used in this study (Table 1). Annual minimum chemistry concentrations were not utilized since these are often below detection limits for cores from the Antarctic interior.

SIE records are from the Australian Antarctic Data Centre (http://data.aad.gov.au) based on satellite-derived observations (http://nsidc.org/data/nsidc-0051.html) from 1979 to the present. Measurements were made on a daily basis (365 samples per year). For our study, values of chemistry concentrations and SIE are calculated over the years from 1979 to the top of the core. We use annual maximum, mean and minimum SIE in degrees latitude for each 10° sector to compare to the chemical species.

Linear correlations are used to examine the relationship between maximum and mean Na$^+$, nssSO$_4^{2-}$ and MS$^-$ concentrations and annual maximum, mean and minimum SIE for each of the 36 10° sea-ice sectors. This routine is applied to the six chemical species for maximum, mean and minimum SIE on all six cores. Correlation results, presented in Figure 3, meet three criteria: (1) the confidence interval is >90%; (2) correlations occur in at least two sectors that are no more than one 10° sector apart; (3) these correlations have the same sign. Application of these criteria results in assemblages of two or more adjacent sectors (20° or more) that contain significant SIE correlations related to an ice-core
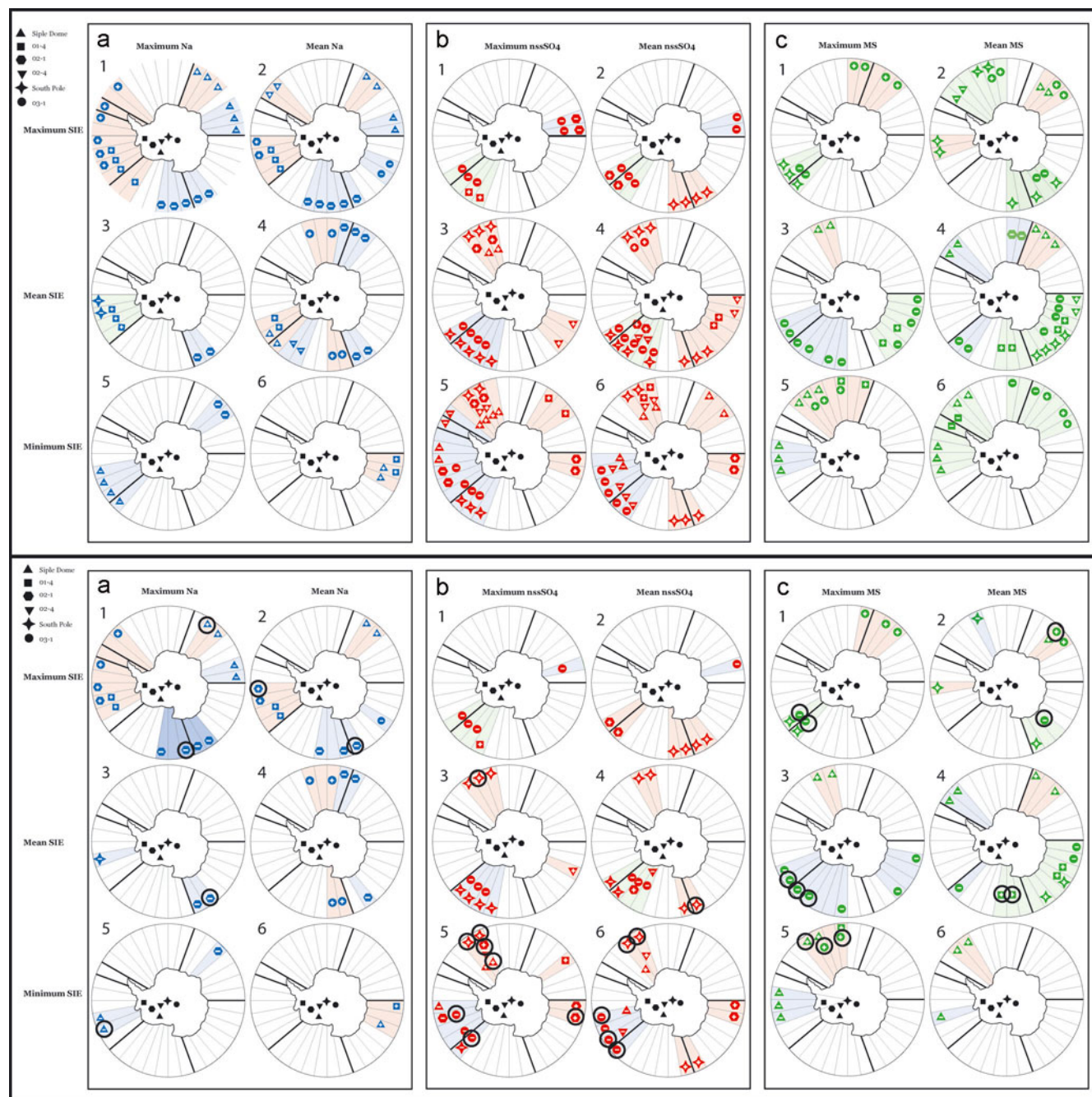
Fig. 3a and b. Linear correlations between maximum, mean and minimum SIE and annual maximum and mean (a) sodium (blue), (b) non-sea-salt sulfate (red) and (c) methylsulfonate (green) for six spatially distributed Antarctic cores. Correlations were calculated for 36 10° sectors around the continent. All plotted values are at or above the 90% confidence interval, and 80% of the assemblages contain a correlation at or above the 95% confidence interval. Only correlations of the same sign in two or more sectors separated by only one sector (10°) are retained. Latitudinal placement of correlation symbol within a sector has no significance. Heavy longitudinal lines group sectors into regions: Indian Ocean (20–90°), Western Pacific (90–160°), Ross Sea (160–230°), Amundsen–Bellingshausen (230–290°), Antarctic Peninsula (290–300°) and Weddell Sea (300–20°).

site. Confidence intervals for each core are given in Table 2. Positive (negative) correlations indicate that increased (decreased) chemistry concentration is associated with increased (decreased) SIE.

Major SIE regions used in this study (Fig. 1) follow divisions developed by Zwally and others (2002) as follows: Indian Ocean (IO, 20–90°), Western Pacific Ocean (WP, 90–160°), Ross Sea (RS, 160–230°), Amundsen–Bellingshausen Seas (AB, 230–290°), Weddell Sea (WS, 300–20°), plus the Antarctic Peninsula (AP, 290–300°; not defined in Zwally and others, 2002).

Table 2. Pearson's confidence intervals at 90%, 95% and 99% for cores in this study

Site	90%	95%	99%
Siple Dome	0.426	0.497	0.623
01-4	0.360	0.423	0.537
02-1	0.345	0.406	0.519
02-4	0.345	0.406	0.519
South Pole	0.360	0.423	0.537
03-1	0.369	0.433	0.549

DISCUSSION

Na$^+$ and SIE

Maximum Na$^+$ and maximum SIE (Fig. 3a, part 1) reveal the greatest number of correlations (21) developed from the Na$^+$ and SIE examination. All SIE sector assemblages contain at least one 10° SIE sector at or greater than 95% confidence interval. Sectors with these correlations are evenly distributed around the continent, and all major sea-ice regions correlate with one or more sites. Signs of the correlations cluster such that all correlations are negative from 60° to 190° and positive from 210° to 50°.

South Pole and 02-4 do not display a maximum-Na$^+$–maximum-SIE correlation (Fig. 3a, part 1) although 02-4 does have mean-Na$^+$–maximum-SIE correlations with the AP–WS region (Fig. 3a, part 2). There is no significant correlation with SIE and mean Na$^+$ at the South Pole (Fig. 3a, parts 3 and 4) as found by Dixon and others (2005) using Na$^+$-derived ssSO$_4{}^{2-}$–SIE correlations. The South Pole exception is particularly interesting because Na$^+$ exhibits a strong seasonal maximum during winter (Cunningham and Zoller, 1981; Whitlow and others, 1992). It is likely that the winter polar vortex centered over Antarctica creates a barrier that isolates the interior from coastal atmospheric influences (Wang and others, 2005), thus removing coastal sea ice as a directly linked source of Na$^+$ to the South Pole in winter. Rather the Na$^+$ may arrive at the South Pole after considerable mixing from multiple transport sites, making it less well correlated to any particular set of sites.

The IO region contains two separate assemblages of sectors that correlate with Siple Dome Na$^+$, but each with the opposite sign. Maximum Na$^+$ correlates positively with maximum SIE from 20° to 50°, but negatively from 60° to 90° (Fig. 3a, part 1). The inverse correlation referred to above is due to the anticorrelation of the SIE data in these regions. When SIE increases (decreases) in the 20–50° sector, it decreases (increases) in the 60–90° area (http://nsidc.org/data/nsidc-0051.html).

Siple Dome correlations in the IO subsectors 30–40° and 70–80° noted above are at the 99% confidence interval ($r = 0.81$ and -0.61, respectively) and the former is the most significant correlation found in this study (Fig. 3, part 1). A negative correlation at >99% confidence is found for site 02-1 with the 160–170° SIE sector ($r = -0.52$) (Fig. 3a, part 1).

NssSO$_4{}^{2-}$ and SIE

Maximum and mean nssSO$_4{}^{2-}$ and minimum SIE correlations (Fig. 3b, parts 5 and 6) are the most numerous in this study (27 and 26, respectively). All core sites reveal these correlations, and all major regions correlate with at least one ice-core site. In general, maximum nssSO$_4{}^{2-}$ correlations in the RS, AB and AP regions are negative and those in the WS, IO and WP are positive. All but four of the correlations are on the western side of the continent. Mean nssSO$_4{}^{2-}$ and minimum SIE positive correlations extend into the western RS and are distributed around the continent similar to maximum nssSO$_4{}^{2-}$.

Unlike Na$^+$ and MS$^-$ that are correlated primarily with only one SIE state (maximum, mean or minimum), nssSO$_4{}^{2-}$ has significant correlations with both minimum and mean SIE. Mean nssSO$_4{}^{2-}$ and mean SIE (Fig. 3b, part 4) are correlated at all core sites except Siple Dome. Of the 25 correlations, 13 are clustered in the western RS region. This western RS group contains all core sites except 01-4 (and Siple

Dome), and all correlations in this region are negative except 02-1. Correlations in WS, WP and WP/RS are all positive.

The Siple Dome and South Pole core site results obtained by Dixon and others (2005) for annual mean nssSO$_4{}^{2-}$ and annual mean SIE correlations are somewhat different from those in this study. There are three differences between the studies. First, and possibly most important, we extended the South Pole record from 1992 to 2000 by stacking data. Second, our sea-ice data start in 1978 rather than 1973, to include only the combined scanning multichannel microwave radiometer and Special Sensor Microwave/Imager (SMMR/SSM/I) satellite data (Parkinson, 2004). Third, there are different approaches to determining annual mean concentrations.

The greatest number of sectors with correlations at or greater than 99% confidence of all the chemistry–SIE states measured in this study is that of the maximum-nssSO$_4{}^{2-}$–minimum-SIE association (seven; Fig. 3b, part 5). Also, the greatest number of core sites with correlations >99% is that of the maximum-nssSO$_4{}^{2-}$–minimum-SIE association (six; Fig. 3b, part 5). The mean-nssSO$_4{}^{2-}$–minimum-SIE association contains the second highest number of sectors at or greater than 99% confidence (five; Fig. 3b, part 6).

MS$^-$ and SIE

Mean MS$^-$ and mean SIE (Fig. 3c, part 4) have the greatest number of correlations (23) using this proxy. All core sites have significant correlations and all major SIE regions correlate with one or more sites with the exception of AB. Distribution of the correlations is heavily weighted to the western half of the continent, with only 4 of the 23 correlations between 180° and 360°. Only four correlations are in the RS region. The precursor of biogenic MS$^-$, DMS, is released during spring sea-ice break-up (Trevena and Jones, 2006), during polynya formation (DiTullio and Garrison, 1995). The RS polynya is the largest and most productive in Antarctica (Arrigo and van Dijken, 2004) and the region is the most productive in the Southern Ocean (Arrigo and others, 1998). It is surprising, therefore, that there is not a stronger correlation for MS$^-$ in the RS for the six core sites in this study. MS$^-$–SIE correlations studied previously in the RS region were the two most significant reported. Welch and others (1993) reported an MS$^-$–SIE correlation coefficient equal to 0.802 for Newall Glacier and the RS. Rhodes and others (2009) reported a Mount Erebus Saddle to RS coefficient of 0.902.

The mean-MS$^-$–mean-SIE correlations in the WP region are very similar to the mean nssSO$_4{}^{2-}$ and mean SIE results in the same region. Core sites 01-4, 02-4, South Pole and 03-1 contain mean-MS$^-$–SIE correlations (Fig. 3c, part 4), and all but 03-1 contain mean-nssSO$_4{}^{2-}$–mean-SIE correlations (Fig. 3b, part 4).

The distribution of the direction of the correlations is extremely varied for mean MS$^-$ and mean SIE (Fig. 3c, part 4). Correlations of Na$^+$ and nssSO$_4{}^{2-}$ to SIE within specific regions are in the same direction at all ice-core sites, suggesting a strong source influence. MS$^-$–SIE correlation signs are distributed more randomly, suggesting a weaker source influence and perhaps stronger site condition influences. Certainly, MS$^-$ is known to migrate after deposition (Mulvaney and others, 1992; Wagnon and others, 1999; Delmas and others, 2003) and accumulation rates affect this migration directly (Curran and others, 2002; Weller and others, 2004).

The WP and RS regions contain the most mean-MS$^-$–mean-SIE correlations above 95% (Fig. 3c, part 4). Core 01-4 contains the only correlations at or greater than 99% confidence in the RS region ($r = 0.62$ and $r = 0.54$, $n = 22$).

DISCUSSION

Processes that lead to the aforementioned correlation patterns occur on temporal scales, spatial scales, are reflective of the source strength and are influenced by site conditions. In this paper, we provide the framework for further investigation and offer some preliminary interpretations.

On a temporal scale, seasonality can be inferred from correlations between chemical species and ice extents. Specifically, maximum SIE occurs in winter/early spring and is most strongly correlated with maximum ice-core Na$^+$. This is consistent with other studies but does not address the question of whether the source of the Na$^+$ is sea salt aerosols or frost flowers.

Minimum SIE is representative of summer conditions and is most highly correlated with nssSO$_4^{2-}$. However, nssSO$_4^{2-}$ is also highly correlated with mean SIE, which does not necessarily have a seasonal association because, by definition, mean is the average of all ice extents. A possible explanation for the two SIE–nssSO$_4^{2-}$ correlations may be significant input of nssSO$_4^{2-}$ during both spring (ice break-up and retreat produces DMS) and summer (increased productivity) seasons.

Spatial distribution of the correlations may be a function of atmospheric circulation patterns. For example, regardless of the source of Na$^+$, greater wind speeds in winter/spring may result in the even distribution of Na$^+$ and maximal SIE correlations around the continent. However, maximum- and mean-nssSO$_4^{2-}$–minimum-SIE correlations are heavily weighted to the western half of the Antarctic seas, and mean-MS–mean-SIE correlations are weighted to the east. These uneven distributions may be due to reduced wind speeds in spring and summer, when these species peak in concentration, and their resultant shorter transport pathways.

The scarcity of significant correlations between MS$^-$ and SIE recorded at these six sites in the highly productive Ross Sea region is unexpected. This lack of association points to the need to use an array of ice-core sites and multiple proxies to better capture all geographic regions. The ice-core MS$^-$ array chosen for this study does not reflect conditions in the RS, probably because atmospheric transport of MS$^-$ to these sites from the RS is confounded in some way.

Distribution of the sign of the correlations may provide information about the relative importance of source strength and site characteristics. Na$^+$ and nssSO$_4^{2-}$ SIE correlations of the same sign are often hghly clustered Generally, correlations between Na$^+$ and maximum SIE are positive in the AB/AP regions. With the exception of one sector adjacent to the AP, nssSO$_4^{2-}$ correlations with mean and minimum SIE are always positive in the WS region and always negative in the sectors bridging the RS/AB regions. Intense clustering may suggest strong source influences and/or strong atmospheric transport pathways with less influence by site conditions. MS$^-$ (mean) SIE correlations are less organized by sign, suggesting that local site conditions might dominate over source strength and/or atmospheric transport efficiency.

Future work will include incorporation of SIE correlations from additional cores around Antarctica. Using this framework of SIE correlations in combination with established atmospheric transport pathways, we will work toward a 360° proxy-reconstruction of Antarctic sea ice prior to the instrumental period.

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