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ARTICLE

Ionic content in an ice core from the West Antarctic Ice Sheet: 1882–2008 A.D.

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ABSTRACT: *The study of atmospheric aerosols through polar ice cores is one of the most common and robust tools for the investigation of past changes in the circulation and chemistry of the atmosphere. Only a few subannual resolution records are available for the development of paleochemical and environmental interpretations. Here, we report the ionic content record for the period of 1882–2008 A.D. in an ice core recovered at the ice divide of the West Antarctic Ice Sheet. The ion concentrations found in the core were determined by ion chromatography on more than 2,000 samples and the basic statistics were calculated for major inorganic and organic ions. The dating of the core layers was based on the seasonality of* SO_4^{2-}, NO_3^-, *and* Na^+, *checked by the identification of the Krakatau (1883), Agung (1963) and Pinatubo/Hudson (1991) volcanic eruption signals. Significant aerosol input events were identified and grouped considering the ions present, their provenance and the season. The ionic balance, together with the decomposition of some origin indicators, showed that 36% of the ionic charge is derived from sea salt aerosols, 13% from mineral dust, and 17% from biogenic marine activity, while 34% are mainly products of chemical reactivity in the atmosphere.*

KEYWORDS: *aerosols; ice core; West Antarctic Ice Sheet; trace analysis; ion chromatography.*

INTRODUCTION

The chemical investigation of polar ice cores is an excellent tool in paleoclimatology, especially due to its wide environmental representation when compared to other existing paleoclimatic techniques. An ice core is a reliable local record of past atmospheric conditions that may be representative for a region. Moreover, it can be especially useful for regions with limited instrumental records. While glaciochemical information for central West Antarctica remains scarce (Steig *et al*. 2009), some reports suggest that in recent decades this portion of the continent has been experiencing important regional climate changes such as increased precipitation and warming (Kaspari *et al*. 2004, Bromwich *et al*. 2012). Furthermore, there is a lack of long-term records useful for improvement of climate models and for assessment within, at least, the time scale of the last two centuries.

The ionic content in snow is widely used to study atmospheric aerosols. The characterization of most ionic variability profiles obtained provides the first understanding to investigate and assess atmospheric aerosols, which in turn are proxies linked with long transport pathways, environmental conditions of source regions, and chemical kinetics in the past atmosphere. Thus, with other trace chemical species, the contents of the main ions found in ice cores are used to provide co-registered paleochemical records.

A part of a high-resolution paleochemical record for the Mount Johns region was obtained from an ice core located near the ice divide of the Pine Island Glacier drainage basin in the West Antarctic Ice Sheet (WAIS). We present in this study the ion chromatography (IC) analytical results from the upper 45.8 m of the ice core, which represent the period from 1882 to 2008 A.D. This core is a contribution of the International Trans-Antarctic Scientific Expedition (ITASE) programme (Mayewski *et al.* 2005), an initiative with the goal of collecting data from the last two centuries in Antarctica.

MATERIALS AND METHODS

For this study, a firn/ice core was collected at coordinates 79º55’28”S, 94º23’18”W and 2,115 m a.s.l., located on the

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WAIS central sector near the Pine Island Glacier drainage basin divide (Fig. 1). Due to the low ice flow rate (approximately 14 m yr^{-1}; Rignot *et al.* 2011), reduced deformation of stratigraphic layers is expected for this site. Annual snow accumulation rates are usually higher than 0.08 m w.e.), enough to ensure a seasonal stratigraphic resolution (Steig *et al.* 2005, Kaspari *et al.* 2004). The core comes from a region that has an interesting pattern of atmospheric circulation caused by the confluence of air masses originating from the Weddell, Amundsen and Bellingshausen Seas (Parish & Bromwich 2007). These were decisive factors in the choice of the core-drilling site indicated in Figure 1 (map of Antarctica).

Sampling

The Mount Johns core was recovered by a Brazilian team from Centro Polar e Climático in the 2008/2009 austral summer. The core was 92 m of firn and ice in 94 sections of approximately 1 m length and 8.5 cm diameter. During the drilling and extraction, the visual stratigraphy was described. The methodology for the core collection, processing, and a description of the visual stratigraphy found, as well as the density profile, are described in Schwanck *et al.* (2016b). All sections were packed in polyethylene bags and placed in Styrofoam boxes for transport at temperatures below -15ºC from the field to the Climate Change Institute at the University of Maine, Orono, USA, to be processed according to the continuous melting with discrete sampling (CMDS) methodology described by Osterberg *et al.* (2006).

The ice core processing consists of preparation, followed by melting and collection of discrete sections, as analysable aliquots. Cutting, thinning, decontaminating and holding the sections in polymethyl methacrylate melter supports followed a stratigraphic and cleaning protocol control (ISO 14644-1) under class 5 laminar airflow hoods in an environment below -20ºC. The melting and sub-sampling occurred entirely within a class 7 clean room equipped with class 5 laminar airflow hoods where sit the collectors (auto samplers) used to separate the co-registered samples for inductively coupled plasma mass spectrometry (ICP-MS) and IC analysis. These samples come from the internal and uncontaminated part of the freshly melted ice core. Melting occurs by contact with a modified Wagenbach-style Ni^{270} controlled heating plate, while drainage tubes extract water by peristaltic pumping (Osterberg *et al.* 2006). The external portion of the ice core was co-sampled in the same way for determination of the stable isotope ratios (δD and $\delta^{18}O$) by the cavity ring-down spectroscopy (CRDS) technique.

The core was fully melted and sub-sampled with a mean stratigraphic resolution of 2.1 cm. ICP-MS and CRDS results have been published elsewhere (Schwanck *et al.* 2016a, 2016b). The samples and blanks in polypropylene vials were stored below -15ºC in a cold room, packed for thermic transport and sent ready to be analysed at the Centro Polar e Climático laboratory in Porto Alegre (Brazil), by an ion exchange chromatography (IEC) system described below.

Analysis by ion chromatography

Anions and cations were here analysed using two Dionex™ conductivity measuring instruments (ICS-2000 and ICS-2100) scaled according a 2-mm column diameter size, coupled on simultaneous injection mode with an auto-sampler. The separation of analytes was performed using gradient concentrations of the eluents passing through their respective columns. We set fixed loops of 250 μL for direct sample injections, considering the load of the expected ionic matrix. To improve detection limits and signal-to-noise ratios, we placed an electrochemical ion suppressor compartment. The obtained background conductivity was always below 1 μS cm^{-1}.

Quality control

The laboratory activities conformed to normative criteria of quality (ASTM D4453), care and control of sample contamination. The lab water reagent (ASTM D1193) must have low and, ideally, constant levels of contaminants. Thus, type I water was always used (>18.0 MΩ cm at 25ºC). The lab materials were defined according to chemical stability tables and internal reproducibility tests at typical working conditions. Materials and tools were previously decontaminated following an internal cleaning protocol. Any direct sample handling was performed under a class 5 laminar-airflow hood installed in a class 7 clean room. The same room conditions were used for the operation of the instruments.

Calibration was performed following Barwick's (2003) guidelines by the method of "external standards". Standard solutions were prepared weekly using stocks of commercial Standard Reference Materials (SRMs) stored at 4ºC or from dissolution of pure salts according to normative ASTM D5542. They were prepared to contain analyte concentration ranges according to the usual composition of the ice matrix samples. The relative standard deviation (RSD) achieved for the calibration curves was lower than 3% for most analytes, except for Ca^{2+} and organic ions, and the achieved linearities, measured by the coefficient of determination (r^2), were usually above 0.9995. Method detection limits (MDL),calculated from the standard deviation of 8 replicates of reagent water fortified with analytes of interest, amounted to less than 0.8 μg L^{-1} for most ions. Higher values were found only for Cl^- (1.0 μg L^{-1}) and Ca^{2+} (2.3 μg L^{-1}). Bias was calculated by the difference between expected and measured mean SRM values. Positive deviations were found

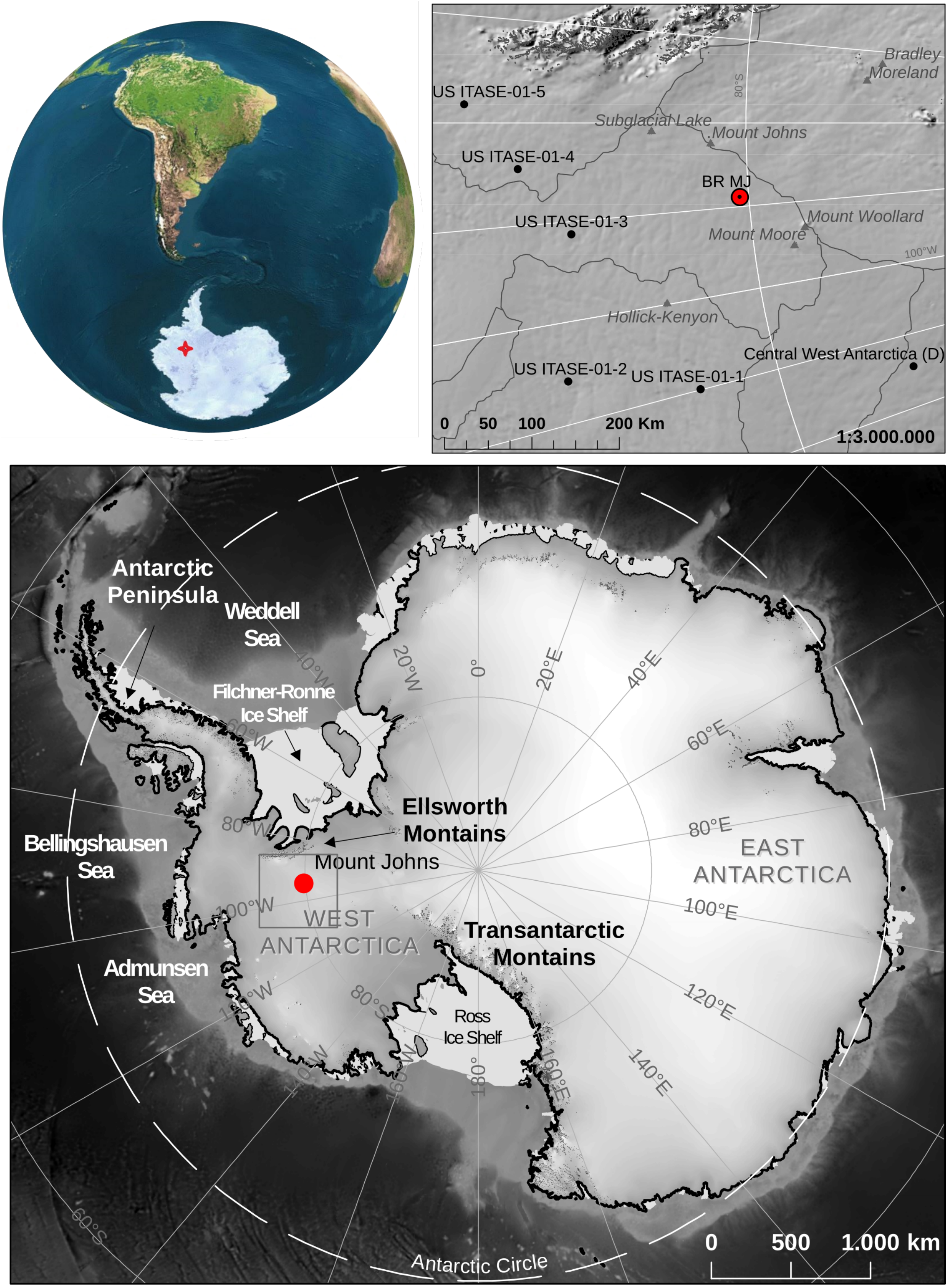

Figure 1. Geographic location of the Mount Johns ice core in (A) and (B). Note other nearby core sites from the ITASE programme and the basin drainage limits detailed in (C).Sources: Cartographic databases from Steig *et al.* (2005), Bamber *et al.* (2009) and the SCAR Antarctic Digital Database (2012).

for all inorganic ions, especially Ca^{2+}, indicating some degree of overestimation on quantification, while negative deviations found for most of the organic ions were associated with losses by chemical degradation, especially for $HCOO^{-}$. Blanks from sub-sampling steps were also analysed, and their replicate means were calculated for subtraction from the analytical datasets.

As dataset treatment, analytical results were tabulated in stratigraphic order, and basic statistical parameters were calculated. Some outliers were identified and disregarded, using as the cut-off criterion the median plus 10σ. The use of medians, instead of means, was considered a preferable central tendency measure due to normality test rejections at $\alpha < 0.05$ level for all profiles, which implies skewed data. Furthermore, medians are less susceptible to influence by outliers.

RESULTS

Schwanck *et al.* (2016a, 2016b) published information on the stratigraphy, physical properties and ICP-MS results for the Mount Johns ice core. Here, we provide co-registered data from the ion chromatography analysis. The main analytes, at trace concentrations in the core matrix, are the major ions Na^{+}, K^{+}, NH_4^{+}, Mg^{2+}, Ca^{2+}, Cl^{-}, SO_4^{2-}, and NO_3^{-} and, additionally, the minor organic acid ions $H_3CSO_3^{-}$, $HCOO^{-}$, H_3CCOO^{-} and $C_2O_4^{2}$. We report the results of the upper 2,164 samples. Basic statistics calculated for each ion dataset are shown in Table 1.

The ionic median concentrations represent each contribution to the bulk ions in the studied period (1882–2008), as a fraction on the mean ion balance. Their sum provides an estimate of the total ionic load average (4.99 μeq L^{-1}). The carboxylic groups $HCOO^{-}$, H_3CCOO^{-} and $C_2O_4^{2-}$ represent less than 5% of the total anionic content estimated, while the major anions compose more than 92%, including Cl^{-} (38%), NO_3^{-} (33%) and SO_4^{2-} (22%). The cation content is essentially acid, with approximately 40% of calculated free acidity, followed by Na^{+} (29%), NH_4^{+} (13%), Mg^{2+} (12%), Ca^{2+} (4%) and K^{+} (1%). The global analytical uncertainty of the total bulk ionic concentration, calculated using a combination of uncertainties from 12 analytes, is estimated at approximately 1.6%. The calcium median (by ICP-MS), extracted from co-registered data in Schwanck *et al.* (2016b), was chosen to represent this fraction over the ionic balance estimation instead of the Ca^{2+} median (by IEC), due to the difference between their analytical consistencies.

Dating

We performed the dating of the record by visual counting of the annual layers (summer-winter variations) in some

Table 1. Basic statistics of ionic profiles from the Mount Johns ice core (central West Antarctica). Amounts in μg L^{-1} (except for H^{+}, in μeq L^{-1}).

Variable	Minimum	Maximum	Mean	Median (Md)	± σ	Cutoff (Md + 2σ)	Sample numbers (N)
Na^{+}	0.2	330.9	24.2	16.6	28.2	72.9	2,157
Mg^{2+}	0.1	28.5	4.8	3.7	3.7	11.2	2,161
Cl^{-}	3.4	390.1	46.3	33.3	43.7	120.7	2,157
SO_4^{2-}	7.5	189.3	30.2	25.9	17.7	61.2	2,161
$nssSO_4^{2-}$	1.2	134.3	24.6	20.5	16.5	53.4	2,123
Ca^{2+}	0.4	23.7	6.1	5.4	3.4	12.1	2,149
K^{+}	0.4	65.8	2.2	1.3	3.7	8.6	2,138
NO_3^{-}	15.4	148.7	53.1	50.8	18.5	87.8	2,161
NH_4^{+}	0.5	53.2	6.1	5.8	4.7	15.2	1,861
$H_3CSO_3^{-}$	0.6	50.1	8.4	7.1	5.4	18.0	2,153
H_3CCOO^{-}	0.3	50.6	4.6	3.4	4.7	12.9	1,861
$HCOO^{-}$	0.4	28.7	2.2	1.7	2.5	6.7	1,860
$C_2O_4^{2-}$	0.5	24.3	1.4	1.1	1.8	4.8	1,861
$H^{+}_{(calc.)}$	0.99	3.68	0.99	0.91	0.67	2.24	2,156

ionic profiles, especially in non-sea salt sulphate (nssSO$_4^{2-}$) and NO$_3^-$ with summer peaks, in antiphase with Na$^+$ (winter peaks), and absolute dating by identifying known volcanic eruption signals that also appear in other Antarctic ice cores (Tab. 2).

The nssSO$_4^{2-}$ was calculated by the difference in amount between the measured SO$_4^{2-}$ and its fraction from sea salt (ssSO$_4^{2-}$), which in turn was calculated considering the proportionality of salts found in mean seawater following the methodology in Dixon *et al.* (2004) and Steig *et al.* (2005). The dating based on the nssSO$_4^{2-}$ stratigraphy profile is illustrated in Figure 2. Note the clear increase in winter minima next to volcanic events. The period covered (1882–2008 A.D.) has relative precision of approximately 1 month and absolute dating less than 2 years, in agreement with results obtained by Steig *et al.* (2005) with a similar methodology for sampling and analysis.

The dating of the layer provides the annual accumulation rate profile, after real depth conversion to water equivalent depth (m w.e.) by multiplying the firn/ice stratigraphy density profile. For this 127-year period, the annual accumulation rate varies from 0.11 to 0.34 m w.e., with a mean of 0.21 ± 0.04 (1σ) m w.e. (see Fig. 3). The analysis of variance shows no significant trend at the $\alpha < 0.05$level. The variability softened by a 5-year fast Fourier transform (FFT) filtered at a 0.1 cut-off shows 2 clear periods of 20 years of accumulation rates below the mean (1900–1920 and 1960–1980), in contrast with the clearly above-the-mean periods 1920–1950 and before 1900 and after 2000 A.D.

Time series of ion variability are shown in Figures 4 and 5. The ionic profiles have been smoothed by 3 adjacent sample averages, except for the Ca^{2+} series, with two passes to reduce noise, as the concentration was determined with a lower precision.

Significant events

An assessment of the ion profiles permits the identification of the highest concentration peaks and their durations.

Table 2. Volcanic SO$_4^{2-}$ signals identified for the period 1882–2008 A.D.

Eruption	Latitude	Event		Signal found			
		VEI*	Start date	Start date	Delay	Duration	Intensity
Krakatoa	6°S	6	08/1883	1884.7	1.0 yr.	3.0 yr.	Strong
Santa Maria	15°N	6	10/1902	1903.9	1.1 yr.	2.1 yr.	Moderate
Agung	8°S	4	03/1963	1964.2	0.9 yr.	2.3 yr.	Moderate
El Chichón**	17°N	5	04/1982	1983,3	1.0 yr.	1.0 yr.	Weak
Pinatubo	15°N	6	06/1991	1992,1	0.6 yr.	2.9 yr.	Moderate
Cerro Hudson	46°S	5	08/1991		0.4 yr.		

*VEI: Volcanic Explosivity Index that compares themagnitude of different volcanic eruptions considering factors such as plume height, bulk of material emitted and eruption duration;**refers to signal not confirmed in other profiles.

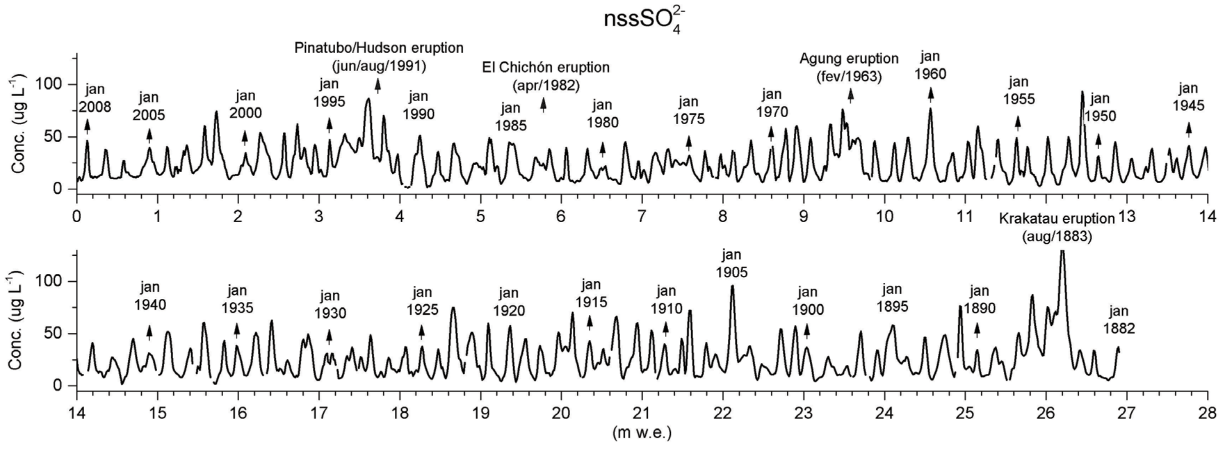

Figure 2. Dating over the non-sea salt sulphate (nssSO$_4^{2-}$) concentrations in the stratigraphy profile obtained from Mount Johns (central West Antarctica). Depth is shown in metre water equivalent (m w.e.), and values are 3 adjacent sample average smoothed.

They are interpreted as important events of ionic load inputs associated with exceptional climatic conditions. These extreme events are identified using as selection criteria values higher than the median plus 2σ in each profile. Events are considered significant if the signals are found at least in three different ion profiles, and they are grouped by types considering the main ions affected, the season and the associated provenance (see Tab. 3).

DISCUSSION

Ionic concentration time series

The basic statistical results in Table 1 are similar to others already published for West Antarctica with similar methodology (*i.e.*,Bertler *et al.* 2005, Dixon *et al.* 2011). Spearman's correlation between Na^+ and Cl^- is 0.96 and between Mg^{2+} and Cl^- is 0.81 at the $\alpha < 0.05$ level. These strong correlations indicate that they have essentially the same source (sea salt), also observed in significant events such as the 1901 and 1933 A.D. winter peaks, especially of Na^+, Mg^{2+} and Cl^-, and probably from advective air masses coming from the Weddell, Amundsen and Bellingshausen Seas. The lower proportions of Ca^{2+} and K^+ in sea salt aerosols also contribute to lower correlations, such as Na^+ with Ca^{2+} (0.23, $\alpha < 0.05$) and Na^+ with K^+ (0.65, $\alpha < 0.05$), or Mg^{2+} with Ca^{2+} (0.21, $\alpha < 0.05$) and with K^+ (0.60, $\alpha < 0.05$). The low correlations with Ca^{2+} are, in part, due to excessive data noise; however, they could also imply another main source, as indicated by the Ca^{2+} correlation with K^+, with a relatively higher result (0.36, $\alpha < 0.05$), suggesting dust mineral aerosols as a common source of Ca^{2+} and K^+.

Mineral dust intake during SE1-type events (Tab. 3) is evident in the Cl^-/Na^+ profile. Ratios lower than the sea salt one (1.8) indicate an excess of non-sea salt Na^+ ($nssNa^+$). These low ratios coincide with peaks of Ca^{2+}, K^+, NH_4^+ and negative values of calculated acidity, all indicative of a contribution from mineral dust. Furthermore, these low ratios also coincide with peaks of sea salt ions, highlighting that the decrease in the Cl^-/Na^+ ratio is not due to Cl^- depletion for these specific events. The Cl^-/Na^+ median ratio is 2.0, slightly higher than the expected 1.8 when mostly sea salt is present, reflecting an excess of Cl^- during summers (probably as HCl), while the Cl^-/Na^+ profile is approximately 1.8 in winter. The acidity profile has summer maxima confirmed with the negative correlations (at $\alpha < 0.05$) with sea salt and mineral dust indicators, such as Na^+(-0.33), K^+ (-0.29), Mg^{2+} (-0.37) and Ca^{2+} (-0.37), which, in turn, increase in winter.

The high correlation between SO_4^{2-} and its $nssSO_4^{2-}$ fraction (0.92 at $\alpha < 0.05$) is due to the prevalence of the latter fraction over the total content. However, $ssSO_4^{2-}$ is also clearly present on the SO_4^{2-} profile, with higher values in significant events of sea salt inputs. Both profiles show clear seasonality with summer maxima, and likewise for NH_4^+ and $H_3CSO_3^-$, indicating an association with marine biogenic sources.

Due to the exclusive production of methane sulphonic acid (H_3CSO_3H) from biogenic marine sources, the presence of intense $H_3CSO_3^-$ peaks with low temporal correspondence with $nssSO_4^{2-}$ suggests other occasional geographic sources of the former, probably from lower latitudes with more active biogenic production. The $nssSO_4^{2-}$ correlations with NO_3^- (0.54 at $\alpha < 0.05$) and H^+ (0.74 at $\alpha < 0.05$) indicate that there is also a positive $nssSO_4^{2-}$ association with the oxidative capacity of the atmosphere, essentially photochemistry, recognized by Wolff (2013) as the main source of NO_3^- in the Antarctic atmosphere. This can be explained by the variation of solar energy inputs that affects both marine biogenic activity and atmospheric photochemistry. Comparing NO_3^- and $nssSO_4^{2-}$, some periods observed have a short delay on NO_3^- signals (approximately 0.2 years), possibly due to post-depositional effects of NO_3^- remobilization within the firn, according Wolff's (2013) hypothesis.

The NH_4^+ profile has low seasonal amplitude (approximately 5 μg L^{-1}) with summer maximum in comparison to its total variability (52.7 μg L^{-1}), which highlights two different sources, one biogenic and other terrestrial, as observed

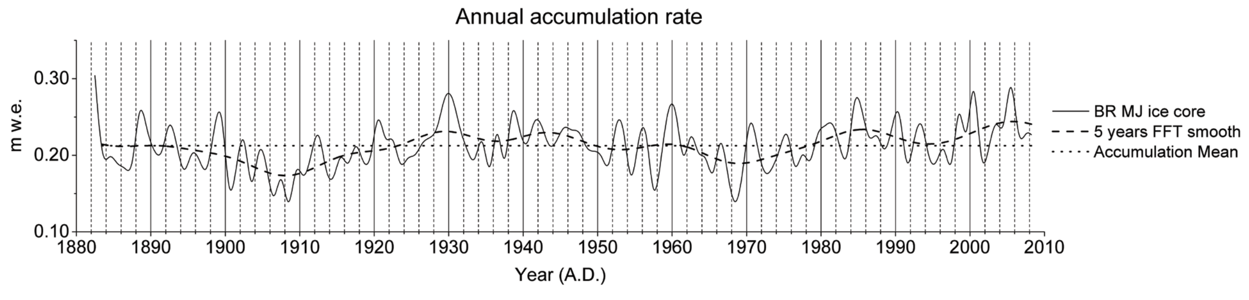

Figure 3. Annual snow accumulation rate from the Mount Johns ice core. Dashed lines are the results after passing a fast Fourier transform considering 5-year intervals. The dotted line represents the mean of the period 1882-2008.

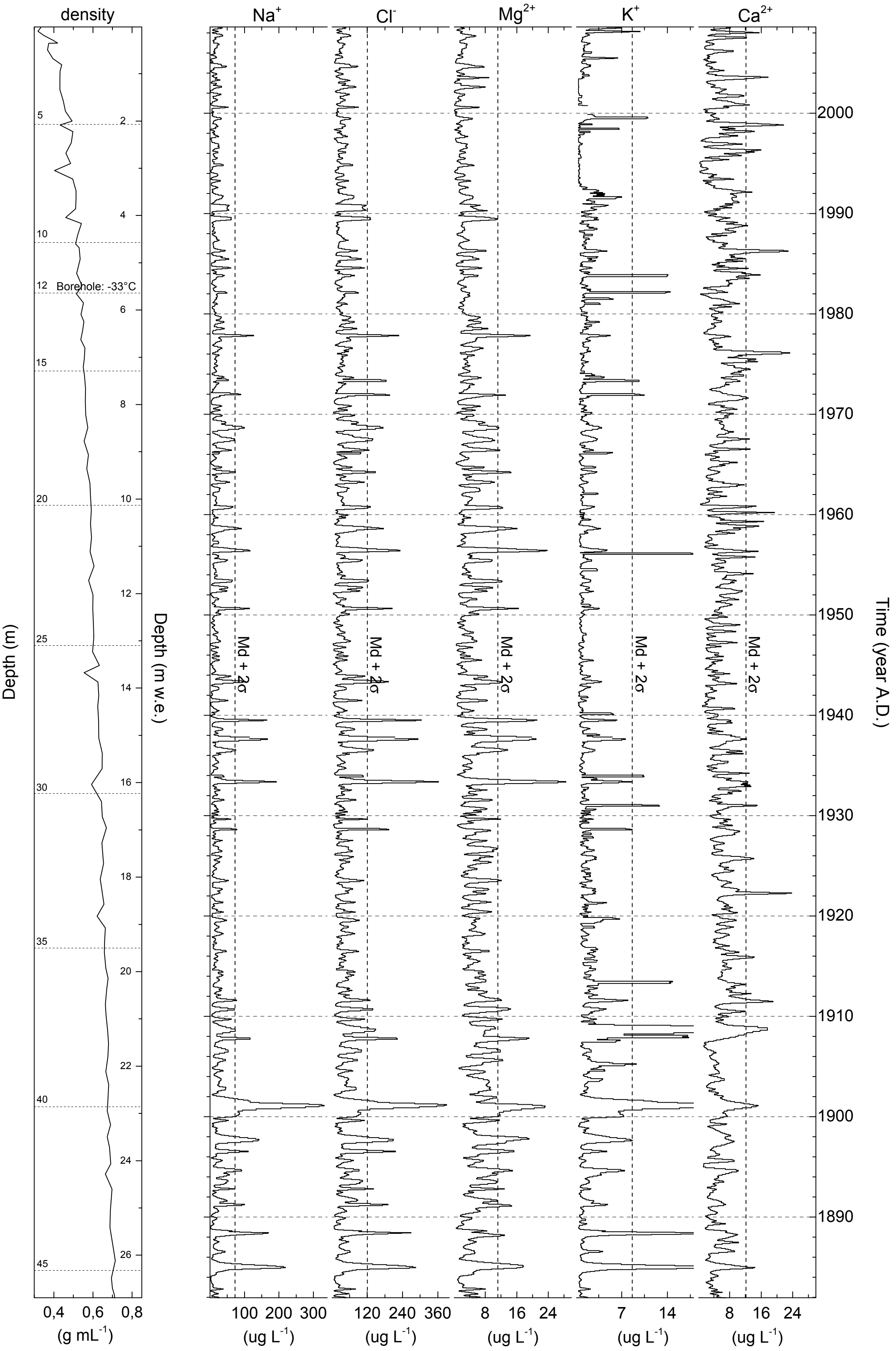

Figure 4. Density, Na^+, Cl^-, Mg^{2+}, K^+ and Ca^{2+} profiles for the upper 45.8 m depth (26.9 m w.e.) of the Mount Johns ice core. Values are 3 adjacent average smoothed. (Continued in Figure 5).

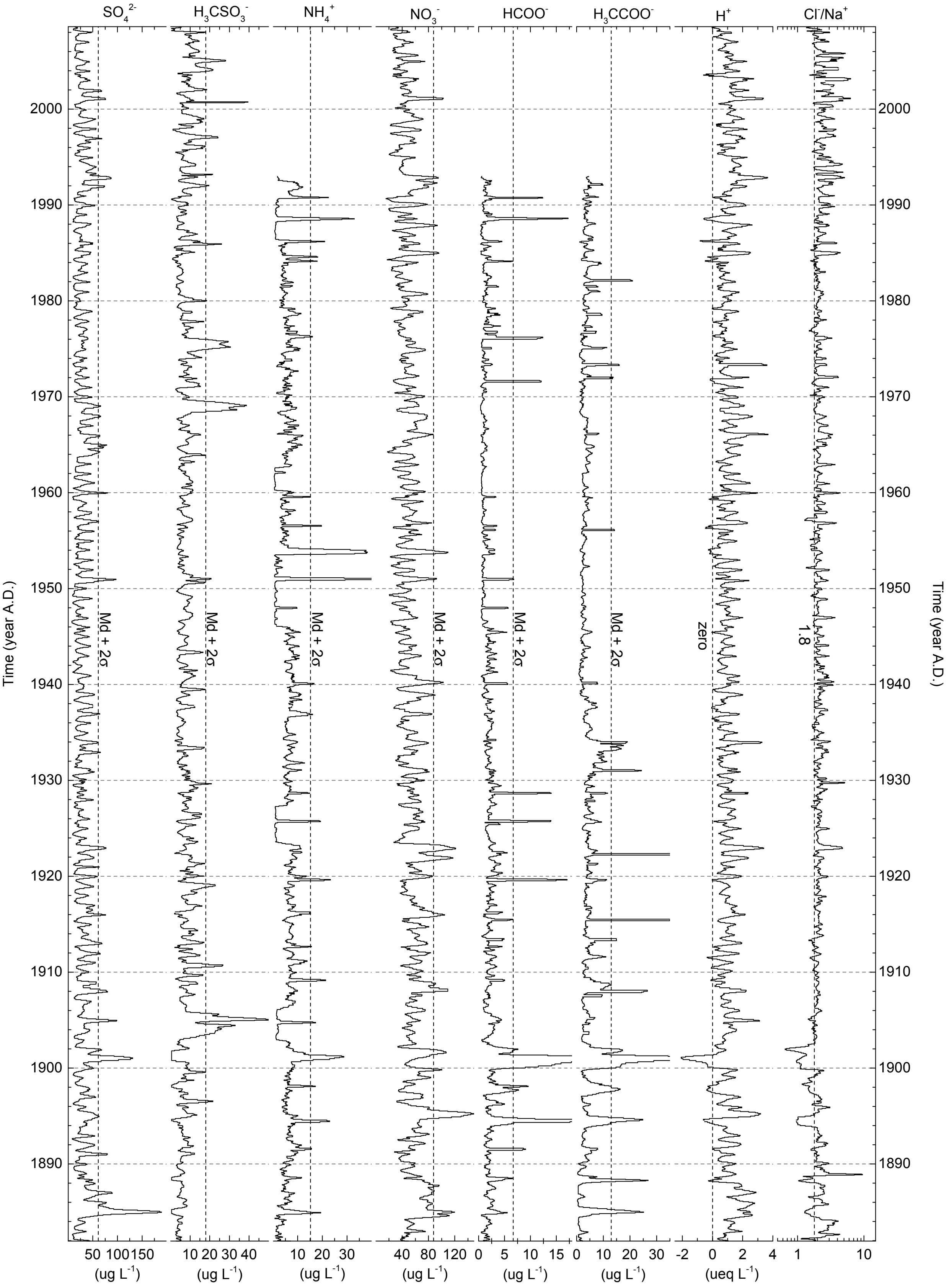

Figure 5. SO_4^{2-}, $H_3CSO_3^-$, NH_4^+, NO_3^-, H_3CCOO^-, $HCOO^-$, the calculated free H^+ and Cl^-/Na^+ ratio profiles for the upper 45.8 m depth (26.9 m w.e.) of the Mount Johns ice core. Values are 3 adjacent average smoothed.

in several higher NH_4^+ peaks that correspond with $HCOO^-$, Ca^{2+} and K^+ and conversely with acidity. The background concentrations of NH_4^+ suffered significant reductions in some periods (see Fig. 5), to amounts close to the method detection limit, and are unexplained to date.

Organic carboxylic acids such as H_3CCOO^-, $HCOO^-$ and $C_2O_4^{2-}$ do not exhibit significant seasonality, although they are essentially products of photochemical activity. The random variability suggests a higher complexity of formation processes in the atmosphere, also considered by Keene and Galloway (1988). The correspondence of the highest peaks is visible between these three profiles; they have different response sensitivities, but, apparently, concentration decreases with increasing molecular chain. They are well marked in SE1-type events; H_3CCOO^- and $HCOO^-$ are especially important for SE2-type events; and SE6-type events are mainly marked by $HCOO^-$. They are products of photochemical activity in the atmosphere in gaseous form and in aerosols, largely found in clouds and precipitation. Their sources within Antarctica are mainly hydrocarbons (basically CH_4) in the gas phase and in trace amounts (Legrand & De Angelis 1995, Legrand & Saigne 1988). Profiles with low seasonal sensitivity, such as these carboxylic acids, can be useful to study time series anomalies of precursor molecules and help to distinguish extreme climatic events.

Ionic content provenance

Quantitative criteria were used to decompose the ions in estimated major source fractions.Na^+, Mg^{2+}, K^+, Ca^{2+}, Cl^- and SO_4^{2-} were first decomposed according the same common source: sea salt aerosol, following the Dickson and Goyet (1994) ion proportions in the calculation of "ss" (sea salt) fractions. Sea salt Na^+ was used as the quantification parameter, because this source is implied in almost 100% of Na^+ found in polar ice cores and because of its conservative properties, according to Kreutz and Koffmann (2013). In this work, we estimate $ssNa^+$, which represents approximately 96% of the total Na^+ measured, by discounting the samples from the measured Na^+ profile that have lower rates than 1.8 in the Cl^-/Na^+ time profile, assuming from other correlations (*e.g.*, Mg^{2+}/Na^+ and Cl^-/K^+) that these samples contain significant amounts of Na^+ from different sources during strong input events.

The results indicate that approximately 51% of Mg^{2+} content, 27% of Ca^{2+}, 47% of K^+, 86% of Cl^- and 15% of SO_4^{2-} measured are from sea salt aerosols, which represents approximately 36% of the total ionic load present during the 1882–2008 A.D. period. In winter, sea salt aerosols are mainly formed by suspension of brine and frost flowers particles over the sea ice cover. Frost flowers are delicate ice crystals rich in salts from precipitation of supersaturated water vapor, with gradual cooling, salinity and crystallization increase. Covering extensive parts of the sea surface, it is a significant source of bulk saline to the atmosphere (Alvarez-Aviles *et al.* 2008). In summer, these aerosols are produced when sea spray droplets are formed over the contact zone between atmosphere and the sea surface (Kreutz & Koffmann 2013). The flux to the atmosphere varies with the wind speed, and its size greatly influences the transport (Jacob *et al.* 1995).

Table 3. Main events identified in the Mount Johns record (grouped in types of classes). SE stands for "Significant Event".

Type	Dates	Main ions	Main characteristics
SE1	1888.5; 1891.3; 1894.7; 1897.7; 1901.1; 1956.4	Na^+, Cl^-, Mg^{2+}, Ca^{2+},NH_4^+, K^+, $HCOO^-$, H_3CCOO^-	Sea salt and mineral dust inputs, associated with low acidity and low marine biogenic activity, in winter.
SE2	1896.5; 1933.4; 1943.4; 1950.8; 1968.8; 1971.8	$H_3CSO_3^-$, Na^+, Cl^-, Mg^{2+}, K^+, $HCOO^-$ H_3CCOO^-, Ca^{2+}	Sea salt inputs, associated with high marine biogenic activity from lower latitudes, in winter. Low correlation between $H_3CSO_3^-$ and $nssSO_4^{2-}$ indicates other geographical sources of $H_3CSO_3^-$.
SE3	1908.0; 1978.0	$H_3CSO_3^-$, Na^+, Cl^-, Mg^{2+}, K^+, $HCOO^-$ H_3CCOO^-, Ca^{2+}, $nssSO_4^{2-}$, SO_4^{2-}.	Sea salt inputs, associated with high marine biogenic activity, in winter.
SE4	1905.0; 1975.0; 1976.0	$H_3CSO_3^-$, $nssSO_4^{2-}$, SO_4^{2-}, NH_4^+	Exceptionally high marine biogenic activity, without sea salt inputs, in summer.
SE5	1885.0; 1964.2; 1992.1	$nssSO_4^{2-}$, SO_4^{2-}, $NO_3^-$and $H_3CSO_3^-$ with negative correlation	Volcanic signal moderate to strong, marked for a duration of 1 to 3 years with increases in winter minima and gradual decreases in intensity.
SE6	1959.4; 1986.3; 1988.6; 2003.6	Ca^{2+},K^+, NH_4^+	Significant inputs of mineral dust, low acidity and low marine biogenic activity, in winter. Lower magnitude events in relation to type SE1.

The calculated non-sea-salt fractions of Mg^{2+} (49%), Ca^{2+} (73%) and K^+ (53%) contents are associated with mineral dust sources, which probably have as counter ions a mixture of oxy-hydroxides, aluminosilicates and carbonates, considering that none of the dissolved mineral dust aerosols consist of irregular particles containing clay minerals, quartz, carbonates, feldspars, sulphates and oxides (Cwiertny *et al.* 2008). We also observe a high correspondence between SE1- or SE6-type events and high NH_4^+ peaks, which suggests terrestrial dust as an important source of $exNH_4^+$ (component of non-seasonal NH_4^+ variation).

Dust particles play an important role as modifiers of the chemical composition of the atmosphere, through water adsorption mechanisms and the formation of deliquescent layers around them, thereby creating in clouds a humid and reactive environment for trace acid gases, mainly H_2SO_4 and HNO_3 (Cwiertny *et al.* 2008). Regarding the insoluble fraction, Cataldo *et al.* (2013) show that 53% of the total identified particles found within an ice core collected at the same site have Si, Al, Fe and Ti as main components and diameters between 1 and 3 μm, compatible with particle sizes transported for long distances. According to Li *et al.* (2008), the main sources of mineral dust deposited in the Austral Ocean and Antarctica are quantitatively Australia and South America. Modelling realized by Li *et al.* (2010) reveals that the origin of dust transport from South America to West Antarctica is mainly the Patagonian semi-desert domain. The meridional fluxes of air masses tend to enter the Antarctic continent, from the west, by travelling over the Antarctic Peninsula and the Ellsworth Lands and, from the east, between Dronning Maud Land andPrincess Elizabeth Land. Therefore, Mount Johns receives air-mass incursions from west and east, according to the flow lines proposed by Parish and Bromwich (2007).

For time series that show clear summer maxima (NH_4^+, $nssSO_4^{2-}$ and NO_3^-), we adopted an empirical and practical criterion to decompose them into two ion sources. The standard deviation (σ) in the period (Tab. 1) was considered as representative of the mean seasonal variability and was directly used as an estimation of seasonal contribution for the content of each ion. In this way, the $exNH_4^+$ contribution was estimated to be approximately 18% of total NH_4^+, and, together with $nssMg^{2+}$, $nssCa^{2+}$ and $nssK^+$, these mineral dust indicators are responsible for 13% of the total ionic load.

The $nssSO_4^{2-}$ fraction has a clear seasonal component "s"(sSO_4^{2-}) that was estimated as 64% of the total SO_4^{2-}. It is mainly associated with biogenic marine activity, in acid form, by the production of SO_4^{2-} as a subproduct of dimethyl sulphide (DMS). Dimethyl sulphide originates from decomposition of dimethyl sulphoniopropionate (DMSP), excreted by living planktonic algae. The regions of the oceans with higher incidence of light and temperatures have higher DMS emission rates to the atmosphere. DMS also accounts for the entire production of H_3CSO_3-, and, therefore, $H_3CSO_3^-$ is considered an unambiguous indicator of marine biogenic production (Seinfeld & Pandis 2016). The $nssSO_4^{2-}$ inputs from volcanic and biogenic sources through the lower stratosphere and upper troposphere (Delmas *et al.* 1982, Legrand 1997) from extra-polar regions also increase in austral summers (due to the weakening of the polar vortex in spring; Thompson & Solomon 2002). Anthropogenic sources are considered negligible by Shaw (1982) andLegrand and Mayewski (1997), which makes Antarctica a useful environment to observe the natural variation of SO_4^{2-} (Dixon *et al.* 2004, Pruett *et al.* 2004). Among the natural $exSO_4^{2-}$ sources are volcanic eruptions (direct release of SO_2) and secondary aerosols formed by oxidation of precursor gases such as SO_2 in the troposphere and the stratosphere (Delmas *et al.* 1982, Legrand & Mayewski 1997, Dixon *et al.* 2004). The $exSO_4^{2-}$ is 21% of the total SO_4^{2-} and represents mainly the background concentration on regional and hemispheric scales.

The natural sources of NO_3^- in the atmosphere are terrestrial, basically NH_4^+ oxidation, biomass burning, soils exhalation and lightning, but Wolff (2013) considers that the main source in polar regions is the formation of secondary aerosols by the photochemical action of NO_x gases. Re-evaporation of NO_3^- and NO_x already stocked on the upper layers of the snowpack makes it difficult to interpret over time, especially in sites with low accumulation rates. Its concentration is a combination of the availability of NO_x precursor gases with the atmospheric oxidation capacity. The hydroxyl radical (OH^-) is the most active molecule that promotes oxidation reactions, which, in turn, influence the residence time of chemical species in trace amounts (Seinfeld & Pandis 2016). Both NO_3^- components (sNO_3^- and $exNO_3^-$) participate actively in secondary aerosol formation and interact with particulate aerosols in the atmosphere; they are subsequently deposited on the snowpack by dry and wet scavenging mechanisms (Wolff 2013).

Median NO_3^- input is high and corresponds to 32% of the total anionic load. To decompose NO_3^-, we consider sea salt provenance insignificant (following Dickson & Goyet 1994), and the nature of NO_3^- sources is not quantified since the formation processes are complex and from multiple sources. However, it is possible to estimate the overall contribution exclusively from seasonal variation (sNO_3^-), produced by photochemical activity, which represents 36% of all NO_3^- quantified and present in the atmosphere mainly in acid, gas and dissolved forms. The excess of NO_3^- ($exNO_3^-$) is the major fraction (64%) of total NO_3^-. In addition to the acid form, salts of NO_3^- can be present due to deliquescence and adsorption around dust particles or by participating in the dechlorinating process of $ssCl^-$ (Legrand & Delmas 1988). Cwiertny *et al.* (2008) point out that mineral dust has a catalytic effect on NO_3^- production in the atmosphere, and the Mount Johns record also shows an association between NO_3^- increases and events of high input of mineral dust, identified as $exNH_4^+$ and $nssCa^{2+}$ in the NH_4^+ and Ca^{2+} profiles.

Other sources associated with the formation of secondary aerosols, which depend on the atmosphere's oxidative reactivity with the presence of trace gas precursors, constitute 34% of the quantified ion load. Figure 6 shows the main ion species measured in this work, their contribution fractions in the ionic balance and some profile components associated with provenance sources.

The free acidity was calculated by the difference between Σ cations and Σ anions, and presuming electrical neutrality. It corresponds to a fraction of approximately 40% of the total anionic load (2,49 μeq L^{-1}). This calculated acidity is considered a minimum and is assumed not to exceed 49%. The extra 9% can be attributed to the overall diverse anionic load contribution, especially derived from mineral dust, and is here estimated by $nssMg^{2+}$ plus $nssCa^{2+}$ (assuming they are a feasible counter-ion mean of a diverse anionic load contribution). The free acidity was also calculated for each sample, generating an acidity time profile that was correlated with other variables for assessment. The acidity profile has clear summer maxima, explained by summer contributions of $H_3CSO_3^-$, sSO_4^{2-} and sNO_3^-, and slightly attenuated by biogenic sNH_4^+ production, with the positive charge competing with H^+ in the ion balance. The light chain carboxylic acids represent 12% of the free acidity, while marine biogenic activity effect ($H_3CSO_3^-$ + sSO_4^{2-} - sNH_4^+) should not exceed 16%. Other sources associated with secondary aerosols by photolytic action of trace gases, reactions with ion adsorption in particles, dechlorinating of sea salt aerosols, re-evaporation of deposits of NO_x and NO_3^-, aerosols transported for long distances in the upper troposphere, or even deposited from the stratosphere, complete the rest of the bulk acidity (72%). They are mostly HNO_3, H_2SO_4 and HCl, already recognized by Delmas and Gravenhorst (1982), Legrand (1987) and others, as the main constituents of the acidity found in Antarctic ice cores.

The participation of CO_3^{2-} in the ionic balance is not considered in this paper, as its contribution is not significant. It is a weak acid and therefore suffers variable and partial dissociation, which also brings methodological difficulties to its evaluation. However, it is feasible to consider the $nssCa^{2+}$ component as an indicator of the maximum CO_3^{2-} contribution from mineral dust and to assume that terrestrial sources of CO_3^{2-} do not exceed the $nssCa^{2+}$ (3%) over the anionic load. They occur predominantly linked (such as $CaCO_3nH_2O$) in mineral structures, for example, as calcite (n=0), monohydrocalcite (n=1) or ikaite (n=6), as suggested by Sala *et al.* (2008).

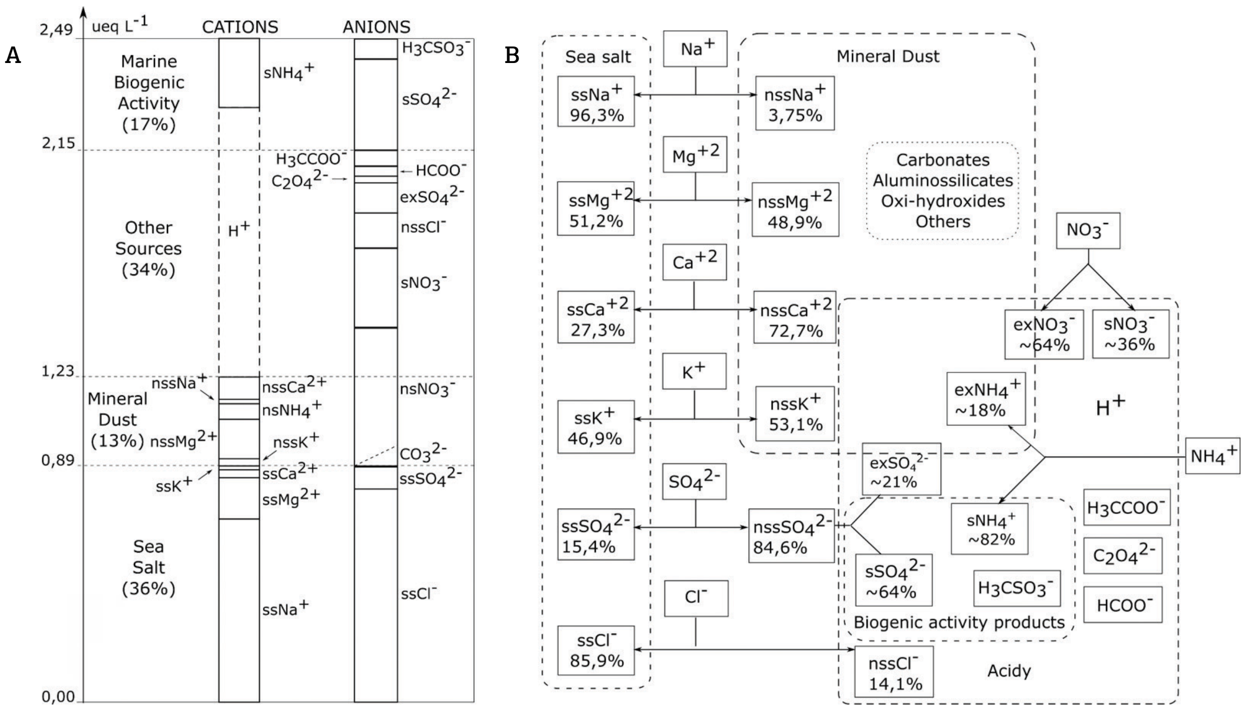

Figure 6. Characterization of the ionic content found in the Mount Johns ice core (central West Antarctica). (A) Detailed ionic balance. (B) Ionic decomposition based on sea salt fractions, standard deviations and medians of time series, and major provenance interpretation.

CONCLUSIONS

The basic statistics for our Mount Johns core correspond with values published for West Antarctica by authors, such as Bertler *et al*. (2005) and Dixon *et al*. (2011). However, the interpretation approach differs from other papers, whereas we present here a more detailed averaged ionic balance and decomposition of the chemistry species that, in turn, was based on stratigraphic profiles standard deviations for seasonality estimation, calculated sea salt fractions and major provenance interpretation according to the literature. We also identify main "significant events" of ionic load input considering the highest concentration peaks and their durations. They were grouped in six types of chemistry and provenance characteristics that were associated with periods of exceptional climatic conditions, such as: sea salt and mineral dust intake associated with low acidity and low marine biogenic activity in winter (SE1-type); sea salt and high marine biogenic activity (SE3-type) or from lower latitudes (SE2-type) in winter; exceptionally high marine biogenic activity in summer (SE4-type); volcanic signals (SE5-type); and high inputs of mineral dust (without sea salt) associated with low acidity and low marine biogenic activity in winter.

The understanding of the origin (transport and formation) of the aerosols found in the region is the main result of this interpretation work based in ion content. Moreover, it is useful for the improvement of climate modelling on the region in future studies. The use of this past atmosphere chemical information for this purpose is the main future objective in the study of the central WAIS region by our group.

In addition, western Antarctica has been experiencing not negligible climate changes in recent decades. The results here presented are useful as a tool to better understand regional air masses patterns that, in turn, subsidize the future study about regional climate changes.

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