Chemical and isotopic profiles from snow pits and shallow firn cores on Campbell Glacier, northern Victoria Land, Antarctica

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ABSTRACT. The chemical (Na^+, K^+, Mg^{2+}, Ca^{2+}, $CH_3SO_3^-$ (MSA), Cl^-, NO_3^-, SO_4^{2-}) and isotopic ($\delta^{18}O$) composition of snow and firn samples from Campbell Glacier, northern Victoria Land, Antarctica, was studied to evaluate the accumulation rate of snow and to investigate the chemical contribution from some emission sources (marine biogenic activity, sea and crust). During the 1994–95 Italian Antarctic Expedition, snow and firn were collected from snow pits and from cores obtained from drilling at three sites (A: 74°41'S, 164°30' E; B: 74°15' S, 164°04' E; C: 73°45' S, 163°20' E), located at 50 m (on the floating glacier tongue), 800 m and 1580 m a.s.l., respectively.

The mean concentration of sea salt decreased with increasing distance from the coast and with altitude. Generally, the Na^+/K^+ and Na^+/Ca^{2+} ratios were much lower than the bulk sea-water ratios at sites B and C. The MSA showed mean concentrations (0.27 and 0.17 $\mu eq\,l^{-1}$ at sites B and C, respectively) consistent with data obtained from other Antarctic sites. The mean concentrations of NO_3^- ranged from 2.1 $\mu eq\,l^{-1}$ (site A) to 0.97 $\mu eq\,l^{-1}$ (site C). The mean nss (non-sea-salt) SO_4^{2-}/SO_4^{2-} ratio was −0.055, 0.54 and 0.42 at sites A, B and C, respectively. Moreover, the relationship between Ca^{2+}, $nssCa^{2+}$, SO_4^{2-} and $nssSO_4^{2-}$ was quite different at sites B and C. In order to explain the relationships between the elements and compounds studied at these sites, chemical fractionation and/or reactions inside air masses and different origin of the air masses at the two sites should be considered.

A comparison of the isotopic and chemical profiles was carried out in order to provide a more reliable chronological scale. The chemical and $\delta^{18}O$ seasonal variations recorded along the firn cores from the upper site of Campbell Glacier seem to be fairly homogeneous. This made it possible to identify many annual cycles (14–18 years for the 7 m firn core). Using the measured density values, the accumulation rate was also calculated for lower and upper Campbell Glacier. It did not appear to differ between the two sites (150–170 kg m^{-2} a^{-1} at site B and 140–180 kg m^{-2} a^{-1} at site C) and is in keeping with rates calculated previously for the same area.

INTRODUCTION

Over the last few years, there has been growing interest in the study of the polar ice sheet, mainly with the aim of reconstructing the interrelationships between the chemistry of the atmosphere and the paleoclimate. Moreover, studies on the mass balance of the Antarctic ice sheet are very important for our understanding of the interrelations between global warming and sea-level changes.

The chemical composition of snow and firn samples from Campbell Glacier, northern Victoria Land, Antarctica, was studied to investigate seasonal signal and chemical contribution from some emission sources (marine biogenic activity, sea and crust). New data on the snow-accumulation rate of Campbell Glacier will improve our evaluation of the mass balance of this glacier.

SAMPLING AND ANALYSIS

A snow pit (2 m deep) was dug in the lower part of the Campbell Glacier tongue (site A: 74°41 S, 164°30' E), about 6.5 km from the cliff, at 50 m a.s.l., during the 1994–95 Italian Antarctic Expedition. Another snow pit (1.4 m) was dug in Campbell Glacier at about 800 m a.s.l. (site B: 74°15' S, 164°04' E), just opposite Mount Campbell and about 50 km from the frontal ice cliff. A firn core (2.37 m) was collected at the bottom of this pit. Finally, another core (7 m) was obtained at 1560 m altitude from the upper sector of this glacier, not far from the confluence of the tributary Recoil Glacier, and about 110 km from the ice cliff (site C: 73°45' S, 163°20' E). Figure 1 shows the sampling map.

Site A, at the glacier tongue, is situated in the percolation zone, where surface melting occurs in the summer. The pit dug in this area revealed many ice layers and pipe-like structures as ice glands. Sites B and C are located in the dry-snow zone of Campbell Glacier, as demonstrated by the temperatures at 3.5 m depth, well below −20°C. Melting does not usually occur here.

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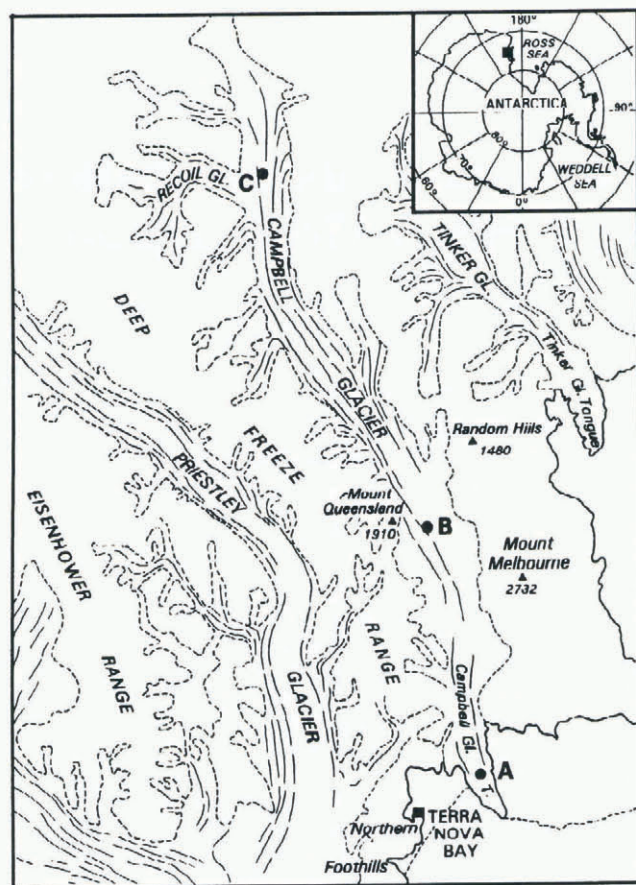
Fig. 1. Map of Campbell Glacier showing sampling sites.

Samples were stored frozen. Then, following surface cleaning in a cold room, they were subsampled and stored in pre-cleaned (with 18 Mohm ultra-pure water) polyethylene containers and sent to the laboratory where they were melted in a clean room prior to the chemical and isotopic analyses.

Density was calculated weighing a measured volume of the snow or firn subsamples analyzed.

Analyses of Na^+, K^+, Mg^{2+}, Ca^{2+}, $CH_3SO_3^-$, Cl^-, NO_3^- and SO_4^{2-} were performed by ion chromatography (Dionex

2020i). Anion separation was obtained by means of a Dionex AS5 column, according to the procedure outlined by Legrand and others (1993). Cation separation was performed using a Dionex CS12 (methane sulfonic acid (MSA) 20 mM eluent). The eluent flow was $1\,ml\,min^{-1}$ and the sample volume was 1.5 ml.

H_2O_2 was analyzed by an electrochemical detector (ANTEC mod. "Decade"), equipped with a micro flowcell (volume $0.005\,\mu l$) with a Pt working electrode (diameter 0.5 mm) in which the potential of the cell was 650 mV. The detector was on line with a pump and chromatograph injection valve. The flow rate of the mobile phase (0.01 M Na_2HPO_4-0.01 N KH_2PO_4 solution) was $0.4\,ml\,min^{-1}$ and the loop was $100\,\mu l$.

The relative repeatability, for all chemical species analyzed, was better than 10%.

The determination of the oxygen isotope composition was carried out according to the technique of isotopic equilibration of CO_2 with water, using an automatic equilibration device (Isoprep 18) on line with an Optima VG mass spectrometer.

The results are reported as δ units per mil (‰) where

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000 ,$$

R being the $^{18}O/^{16}O$. The $\delta^{18}O$ values are reported vs Vienna Standard Mean Ocean Water isotopic standard. The standard deviation of oxygen measurements for the automatic preparation device was equal to an average of ± 0.10‰.

RESULTS AND DISCUSSION

Chemistry of firn

The mean concentration of the ions analyzed is given in Table 1. The concentration of the elements derived from sea salt (typically Na^+, Mg^{2+} and Cl^-) decreased rapidly from the coast to the higher altitudes. This feature has already been described for different Antarctic sites by Herron and Langway (1979), Legrand and Delmas (1985), Mulvaney

Table 1. Concentrations of studied samples

	Na^+	K^+	Mg^{2+}	Ca^{2+}	MSA	Cl^-	NO_3^-	SO_4^{2-}	$nssSO_4^{2-}$	H_2O_2
	$\mu eq\,l^{-1}$	$\mu eq\,l^{-1}$	$\mu eq\,l^{-1}$	$\mu eq\,l^{-1}$	$\mu eq\,l^{-1}$	$\mu eq\,l^{-1}$	$\mu eq\,l^{-1}$	$\mu eq\,l^{-1}$	$\mu eq\,l^{-1}$	$\mu g\,l^{-1}$
Campbell Glacier tongue (50 m a.s.l., site A)										
Mean	1750	34	350	100	0.18	1570	2.1	564	354	31
Std dev.	2890	49	530	153	0.18	2240	2.6	1440	1140	22
Min.	116	3.3	16	7.1	0.05	135	0.6	6	−373	9
Max.	11930	180	2010	640	0.69	7770	11	6380	4950	100
n	21	21	21	21	12	20	14	21	21	16
Campbell Glacier (800 m.a.sl., site B)										
Mean	39.3	4.9	8.9	10.2	0.27	48	1.3	11.4	6.7	8.4
Std dev.	29.3	7.2	5.1	6.9	0.21	32	1.0	7.2	5.7	12.6
Min.	7.2	0.5	2.4	2.2	0.05	14	0.3	2.1	−8.3	0.01
Max.	210	55.2	33.0	40.5	1.32	209	7.2	37.8	28.7	41.2
n	85	85	85	85	83	85	85	85	85	60
Campbell Glacier (1560 m a.s.l., site C)										
Mean	21.1	3.7	3.7	4.1	0.17	22.8	0.97	3.8	1.3	8.5
Std dev.	27.2	4.9	5.0	2.7	0.13	29.7	0.42	3.3	1.6	10.7
Min.	0.9	0.2	0.7	0.9	0.04	2.5	0.20	0.9	−5.7	0.4
Max.	201	32.4	38.4	20.1	0.75	194	3.06	20.4	8.5	48.1
n	156	155	156	156	154	156	156	156	156	154

and others (1993), Minikin and others (1994) and, in the case of northern Victoria Land, by Piccardi and others (1994, 1996) and Caprioli and others (1997).

The higher sea-salt concentration resulting for the Campbell Glacier tongue, about 6 km from the ice edge, is mainly due to dry deposition of large particles from sea-salt aerosol during sea storms (Fig. 2). This process has been observed, for example, at the Filcher–Ronne Ice Shelf (Minikin and others, 1994). The event recorded in the firn layer at about 40 cm depth at site A could be attributed to the storm that struck the Ross Ice Shelf and then moved toward the Transantarctic Mountains at the beginning of June 1993. The wind storm was so severe that some of the automatic weather stations on the Ross Ice Shelf were damaged (Stearns and others, 1994).

In the analysis of the correlation between Na^+ and Cl^-, the equations of the regression lines were $Cl^-\ \mu eq\,l^{-1} = 2.02 + 0.99Na^+\ \mu eq\,l^{-1}$ ($r = 0.99$, $n = 156$) for site C, and $Cl^-\ \mu eq\,l^{-1} = 6 + 1.07Na^+\ \mu eq\,l^{-1}$ ($r = 0.98$, $n = 85$) for site B, both near the dilution line of bulk sea water ($Cl^-/Na^+ = 1.17$). These results suggest, over the overall dataset, an absence of significant fractionation of the reaction products (HCl and Na_2SO_4) between $NaCl$ and H_2SO_4 (Legrand and Delmas, 1988). Nevertheless, some samples showed a significantly higher or lower Cl^-/Na^+ ratio with respect to the Cl^-/Na^+ ratio in sea water. This confirms that in particular conditions fractionation of HCl and Na_2SO_4 may occur.

The equation of the regression line resulting for site A was $Cl^-\ \mu eq\,l^{-1} = 239 + 0.72Na^+\ \mu eq\,l^{-1}$ ($r = 0.95$, $n = 21$), indicating a significantly lower Cl^-/Na^+ ratio with respect to the sea water. This is due to an enrichment of Na_2SO_4 as shown from data obtained from snow samples collected at about 35 cm depth. The $nssSO_4^{2-}$ profile ($nssSO_4^{2-} = SO_4^{2-} - 0.12Na^+$, where all species are in $\mu eq\,l^{-1}$) at site A is provided in Figure 2.

The mean Na^+/Mg^{2+} ratios were 5.1, 4.4 and 5.4 for sites A, B and C, respectively, which are close to the sea-water Na^+/Mg^{2+} ratio (4.14) according to Ikegami and others (1994) and McInnes and others (1994). They found no fractionation of Mg^{2+} relative to Na^+ in aerosol collected from a remote marine boundary layer or the upper tropical troposphere. Nevertheless, in some samples an Na^+/Mg^{2+} ratio higher than the sea-water ratio was observed, suggesting sporadic depletion of Mg^{2+} relative to Na^+. This is in keeping with the results of Mulvaney and others (1993), in a study of the fractionation of sea salt during transport across an Antarctic ice shelf.

Generally speaking, the Na^+/K^+ and Na^+/Ca^{2+} ratios were much lower than the bulk sea-water ratios at sites B and C. The percentages of $nssK^+$ ($nssK^+ = K^+ - 0.0213Na^+$, where all species are in $\mu eq\,l^{-1}$) and $nssCa^{2+}$ ($nssCa^{2+} = Ca^{2+} - 0.043Na^+$, where all species are in $\mu eq\,l^{-1}$) with respect to the total content of these ions were 72.8% and 81.8% at site B and 82.6% and 81.4% at site C. These percentages, which are comparable to those reported by Whitlow and others (1992) at the South Pole, confirm a prevailing crustal origin of K^+ and Ca^{2+}.

The MSA, produced in photo-oxidation of dimethyl sulfide, which is, in turn, derived from the biologically produced precursor, dimethyl sulfonipropionate (Dacey and Blough, 1987), showed mean concentrations (0.21 μM) consistent with data obtained at other Antarctic sites (Ivey and others, 1986; Saigne and Legrand, 1987; Prospero and others, 1991; Legrand and others, 1992; Mulvaney and others, 1992; Minikin and
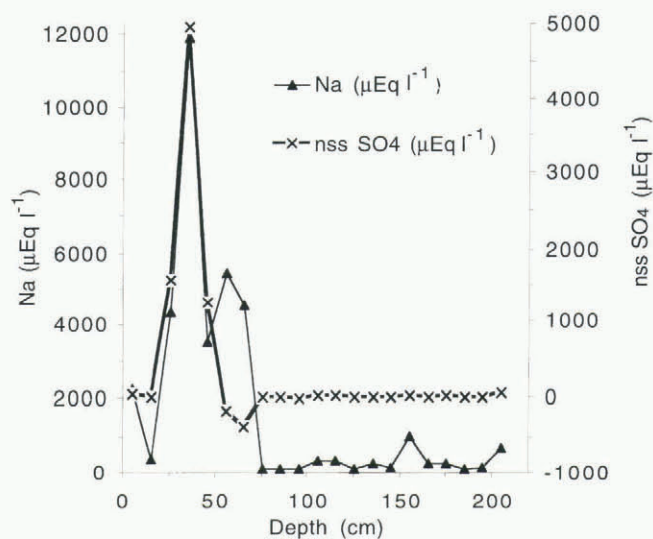

Fig. 2. Na^+ and $nssSO_4^{2-}$ profile at site A.

others, 1994). If the data for the Campbell Glacier tongue are not considered, because of the low number of samples analyzed (12), in which winter samples with lower MSA content could prevail, a decreasing concentration of MSA is observed as altitude increases. The mean concentrations of MSA were 0.27 and 0.17 μM for sites B and C, respectively.

NO_3^- is produced in the oxidation of NOx. In Antarctica, the most important sources of NOx are lightning and transport from the stratosphere–troposphere. Soil release, biomass burning, fossil-fuel burning and volcanic emission are not considered significant sources of NOx (Herron; 1982; Legrand and Delmas, 1986).

The mean concentrations of NO_3^- ranged between 2.1 $\mu eq\,l^{-1}$ (site A) and 0.97 $\mu eq\,l^{-1}$ (site C). These values are consistent with the data reported for other Antarctic sites (Neubauer and Heumann, 1988; Legrand and Kichner, 1990; Qin Dahe and others, 1992; Whitlow and others, 1992; Minikin and others, 1994; Piccardi and others, 1994; Caprioli and others, 1997).

The contribution of sulfate in the Antarctic region is mainly due to marine biogenic activity and sea salt. Crustal and antropic sources are generally negligible. Volcanic events can produce a significant input of SOx into the atmosphere, which can increase SO_4^{2-} deposition and yield a very marked signal in the snow, at sites either close to or far from eruptions (Hammer, 1977, 1985; Delmas and others, 1985; Moore and others, 1991).

In our samples, the mean $nssSO_4^{2-}/SO_4^{2-}$ ratios were −0.055, 0.54 and 0.42 at sites A, B and C, respectively. Negative values of $nssSO_4^{2-}$ can be found (especially at coastal polar sites and in winter) due to little-known processes that lead to an SO_4^{2-}/Na^+ ratio lower than that of bulk sea water. The low $nssSO_4^{2-}/SO_4^{2-}$ ratio at site A confirms the strong marine influence that decreases sharply away from the sea. The $nssSO_4^{2-}/SO_4^{2-}$ correlation was highly significant ($r = 0.88$, $n = 85$) for site B, but less significant for site C ($r = 0.26$, $n = 156$). Moreover, the relationship between Ca^{2+}, $nssCa^{2+}$, SO_4^{2-} and $nssSO_4^{2-}$ at sites B and C differed considerably. At site B, $nssSO_4^{2-}$ and $nssCa^{2+}$ are significantly correlated ($nssCa^{2+} = 2.36 + 0.92nssSO_4^{2-}$; $r = 0.84$), and a large part of the $nssCa^{2+}$ could be in $CaSO_4$ form, whereas at site C, $nssSO_4^{2-}$ and $nssCa^{2+}$ were not correlated ($nssCa^{2+} = 3 + 0.33nssSO_4^{2-}$; $r = 0.08$) (Fig. 3). The $nssCa^{2+}/nssSO_4^{2-}$ ratios (excluding the negative values of nss SO_4^{2-}) were 1.41

and 3.73 at sites B and C, respectively, due to a relatively lower content of $nssSO_4^{2-}$ with respect to other constituents at site C. This low content of $nssSO_4^{2-}$ is also perceptible in other ratios such as $MSA/nssSO_4^{2-}$ (0.092 and 0.26 at sites B and C, respectively).

H_2O_2 is produced in the atmosphere by photochemical processes which reach their maximum intensity during the summer months. Therefore, the atmosphere and snow show a peak in H_2O_2 concentration during this period. Due to this pattern, H_2O_2 is used as a seasonal tracer. The mean concentration of H_2O_2 was 8.45 and 8.5 $\mu g\,l^{-1}$ at sites B and C, respectively. This suggests that the deposition processes at these two sites do not differ.

In order to explain the relationship between the elements and compounds studied from sites C and B, chemical fractionation and/or reaction inside air masses, and the different origin of the air masses at the two sites should be considered. The peculiar chemical characteristics of the firn at sites B and C, and particularly the sharp decrease in $nssSO_4^{2-}$, cannot be justified by the fractionation of chemical species alone. Thus, the contribution of masses of air of different origin should be taken into consideration for sites B and C.

Stable-isotope analyses

The paleotemperature profiles derived from the $\delta^{18}O$ and δD data obtained from the long ice cores obtained in Greenland and Antarctica, are long-standing evidence of the importance of determining the stable-isotope composition of ice cores. In fact, as initially observed by Dansgaard (1964), oxygen and hydrogen isotopic values are related to several meteorological parameters such as the condensation temperature, the cooling processes (i.e. isobaric or adiabatic), the initial isotopic composition of vapor and the trajectory followed by the air masses. As a consequence, linear relationships have been observed in different Antarctic areas linking the mean annual isotopic composition of precipitation to the mean annual surface temperatures (Lorius and Merlivat, 1977; Peel and Clausen, 1982; Isaksson and Karlén, 1994). Decreasing values of the isotopic composition would be observed as one moves inland throughout Antarctica, according to the above considerations.

The stable-isotope composition profile of a firn core can be seen as a temporal record of data that reach their least negative values in summer and their most negative ones in winter, allowing one to establish a chronological scale and to evaluate the mean accumulation rate characterizing the area during the time period considered. In areas where the accumulation rate is very low, homogenization processes may play an important role in the uppermost part of the snow column, as pointed out by Johnsen (1977), totally or partially obliterating the pristine seasonal signal. This is particularly true inland on the Antarctic ice sheet. Obviously, melting at the surface and percolation through the snow-pack and refreezing may also be important factors. Another external factor which can contribute to the obliteration of the original signal is the redistribution of the snow by the wind, which can be very effective in some Antarctic regions. Nevertheless, a tentative chronological scale can be established whenever all these phenomena seem to be less evident.

At site A, $\delta^{18}O$ values ranged between −18.2‰ and −32.9‰, with a mean value of −23.9‰. The almost complete obliteration of the seasonal signal at this low-elevation site
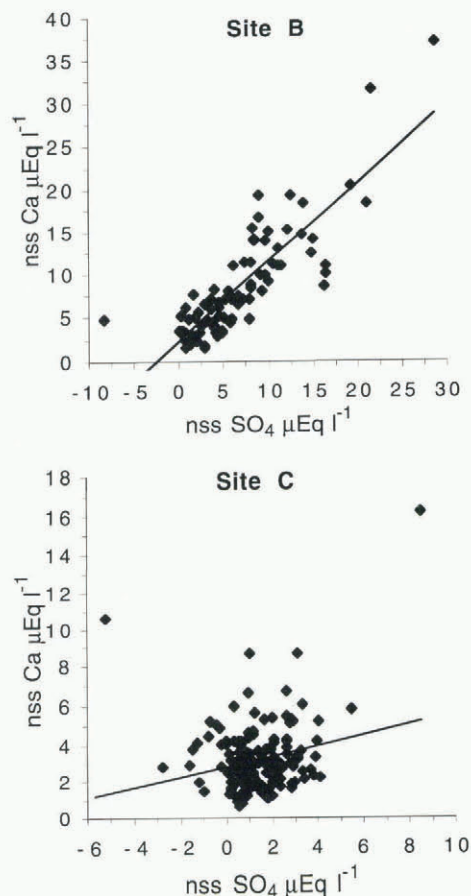

Fig. 3. $nssSO_4^{2-}-nssCa^{2+}$ correlations at sites B and C.

may be due to surface melting occurring in summer. As regards the intermediate-elevation site B, the isotopic values ranged from −23.5‰ to −35.9‰, with a mean value of −27.2‰. In addition, the seasonal signal did not appear to be well preserved in this case and it is quite difficult to explain the smoothed profile by melting processes occurring at the surface in view of the preservation of the chemical seasonal signal in the same core. The explanation may be a redistribution created by the wind, or perhaps a problem with the storage of the core samples. Only one of the chemical parameters, H_2O_2, exhibited a similar pattern, which may support the second hypothesis.

A totally different situation was observed in the case of the higher-elevation site C. Here the seasonal signal record was fairly well preserved, the least negative values being ascribed to the summer precipitation and the most negative ones to the winter period. The $\delta^{18}O$ values ranged from −27.2‰ to −40.8‰, with a mean value of −33.5‰. The variation of the oxygen-isotope composition with depth is shown in Figure 4, along with the chemical profiles.

Comparing the mean $\delta^{18}O$ values for the three cores obtained at different altitudes, and assuming these values represent approximately the mean $\delta^{18}O$ of precipitation at each site, a mean isotopic vertical gradient of −0.6‰ $(100\,m)^{-1}$ can be observed along the glacier axis (−0.4‰ $(100\,m)^{-1}$ between 50 and 800 m, and −0.8‰ $(100\,m)^{-1}$ between 800 and 1560 m). Similarly, a mean "continental" gradient of −0.1‰ km^{-1} was obtained, the more negative values being found inland. These gradients are acceptable and lie within the range of values already reported in the literature (Dansgaard and others, 1973; Qin Dahe and others, 1994); they were previously measured by the authors
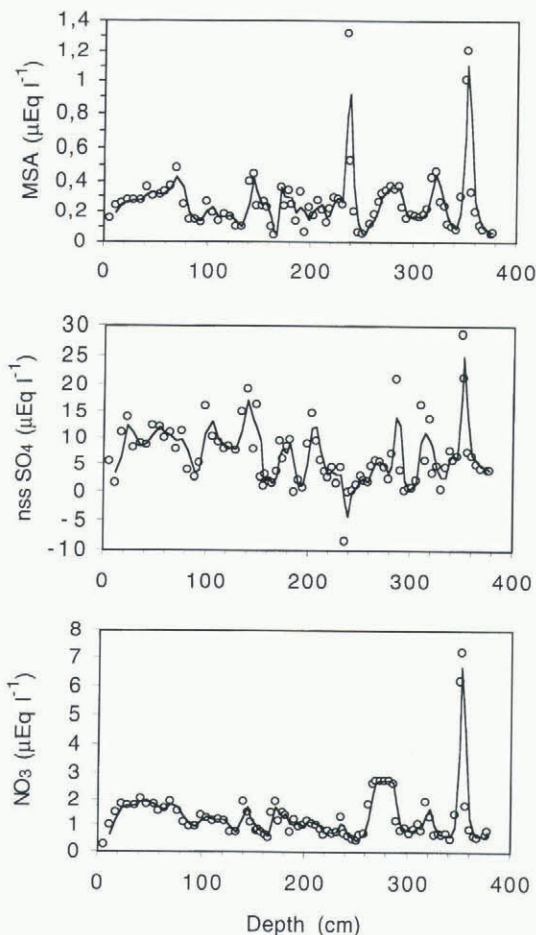
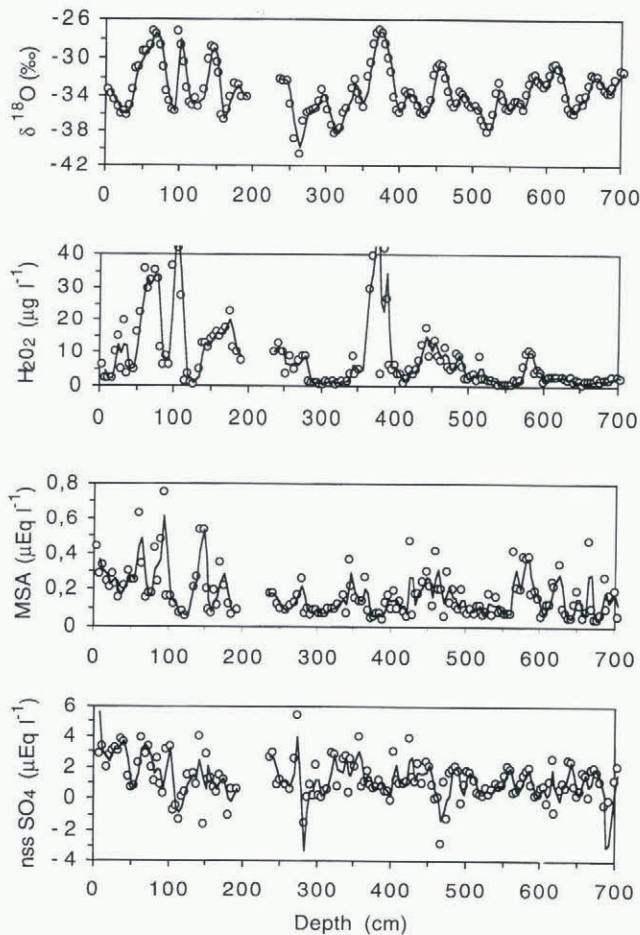Fig. 4. Profiles of chemical species at site B.

Fig. 5. Profiles of isotopic and chemical species at site C.

in the Terra Nova Bay area. Using the Lorius and Merlivat (1977) relationship, $\delta^{18}O = 0.755t\ (^{\circ}C) - 7.6$ (valid for East Antarctica), a mean temperature–elevation gradient of $-0.8^{\circ}C\ (100\ m)^{-1}$ may be calculated.

SEASONAL TREND OF CHEMICAL SPECIES

Unfortunately, the isotopic and H_2O_2 profiles obtained at sites A and B cannot be used for dating purposes due to partial obliteration of the seasonal signal.

Figure 4 shows the chemical profiles for MSA, NO_3^- and $nssSO_4^{2-}$ at site B, and Figure 5 shows the profiles for $\delta^{18}O$, H_2O_2, MSA, $nssSO_4^{2-}$ and NO_3^- at site C. All species showed numerous well-defined annual cycles in which the $\delta^{18}O$, H_2O_2, MSA, $nssSO_4^{2-}$ and NO_3^- peaks correspond to the late-spring–summer period.

When using chemical species profiles to date snow layers, some of the greatest difficulties are related to the inaccurate overlapping of the different profiles. To solve this problem, Udisti (1996) suggests a method involving a sum of normalizing profiles. In this study, we have restricted the data analysis, plotting depth vs chemical species concentrations by a cubic-spline function (Figs 4 and 5) and then plotting depth, corresponding to different years for different chemical species, vs year (Fig. 6, for site C only). In this manner, the differences emerging from the different chemical species profiles can be easily noted.

The number of summer peaks identified according to the chemical and isotopic profiles is given in Table 2.

Taking the mean density (site B = 0.46, site C = 0.384) into account, the mean accumulation rate was within the range 150–170 kg m^{-2} a^{-1} at 800 m a.s.l., where 10 or 11 years of snow accumulation were identified, and within the range 140–180 kg m^{-2} a^{-1} at 1560 m a.s.l., where 14–18 years of snow accumulation were identified. These values are in keeping with those found by Udisti (1996) in the Terra Nova Bay area, whereas Zanon (1989), on the basis of glaciological
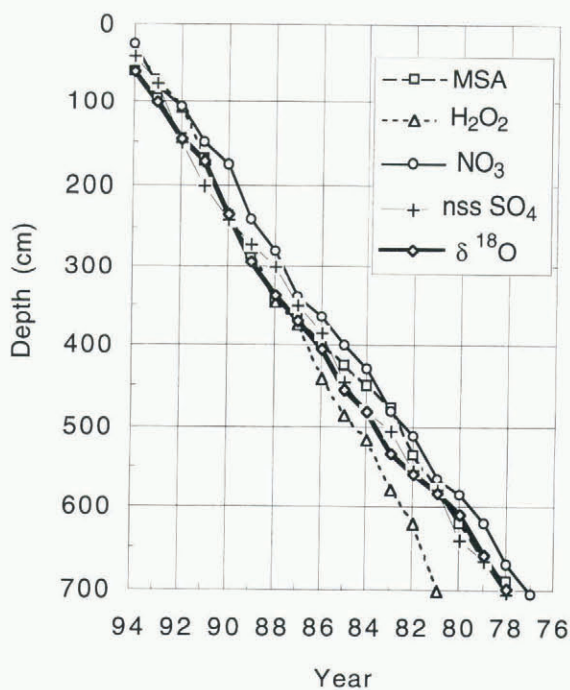

Fig. 6. Chronological profile derived from the concentrations of different chemical species at site C.

considerations, proposed an accumulation rate of 200 kg $m^{-2} a^{-1}$ at the Campbell Glacier tongue.

CONCLUSIONS

The chemical composition of the snow and firn samples from Campbell Glacier confirms the decrease of sea-salt concentration with higher altitudes and increasing distances from the sea. The mean concentration of Na^+, for instance, fell sharply from 1750 μeq l^{-1} at site A (with a maximum of 11900 μeq l^{-1}, an unusually high level, probably due to a strong sea storm) to 39 and 21 μeq l^{-1} at sites B and C, respectively, where the maximum values only slightly exceeded 210 μeq l^{-1}.

Table 2. Number of summer peaks identified at sites B and C

	MSA	NO_3	SO_4	H_2O_2	$\delta^{18}O$
Site B[*]	10	10	11		
Site C	15	15	18	18	19

[*] 1994–95 summer peak was not identified.

The concentration of many of the studied elements and compounds (particularly $\delta^{18}O$, H_2O_2, MSA, $nssSO_4^{2-}$ and NO_3^-, at site C) offers a good seasonal signal, showing higher content during the late-spring–summer period. It was therefore possible to identify many annual cycles (14–18 years for the 7 m firn core). By means of the measured density values, the accumulation rate was also calculated for lower and upper Campbell Glacier. It did not differ much between the two sites (140–170 kg $m^{-2} a^{-1}$ at site B and 140–180 kg $m^{-2} a^{-1}$ at site C) and is consistent with the rates previously calculated for the same area.

ACKNOWLEDGEMENTS

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