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CHEMICAL PROFILES FROM SNOW PITS AND SHALLOW FIRN CORES AND SNOW ACCUMULATION ON CAMPBELL GLACIER (NORTHERN VICTORIA LAND, ANTARCTICA)

ABSTRACT: CAPRIOLI R., GRAGNANI R., GUGLIELMIN M., SMIRAGLIA C., PROPOSITO M. & TORCINI S., *Chemical profiles from snow pits and shallow firn cores and snow accumulation on Campbell Glacier (Northern Victoria Land, Antarctica)*. (IT ISSN 0391-9838, 1997).

The chemical composition of snow and firn samples from the Campbell Glacier (Northern Victoria Land) was studied to evaluate the accumulation rate of snow and to investigate the chemical contribution from some different emission sources (marine biogenic activity, sea and crustal). Snow and firn were collected from snow pits and by coring at three sites (74°41' S-164°30' E; 74° 15' S-164°04' E and 73 45' S-163° 20' E), located respectively at 50 m (on the floating glacier tongue), 800 m and 1560 m a.s.l., during the 1994-95 Italian Antarctic Expedition.

Analyses of Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, CH₃SO₃⁻ (Msa), Cl⁻, NO₃⁻, SO₄⁼⁼ were performed by ion chromatography (Dionex 2020i). The separations were obtained with ion-exchange columns Dionex AS5 (NaOH 5 10⁻⁴ N and NaOH 3 10⁻² N eluents) and Dionex CS12 (methane sulfonic acid 20 mM eluent) for anions and cations respectively. H₂O₂ was analyzed by an electrochemical detector (Antec mod. «Decade»).

Samples from the Campbell Glacier Tongue are characterized by a high level of sea salt and in the upper part of the firn layer a high concentration of nss SO₄⁼⁼ is present. The concentration of sea salt decreases with increasing distance from the coast and with altitude. The differences in the chemical composition of firn at the sites at 800 m and 1560 m altitude could be explained by coupling fractionation of chemical species and air masses of different origin.

Msa, H₂O₂, nss SO₄⁼⁼, NO₃⁻ and nss Ca⁺⁺ profiles show fairly good seasonal cycles. 10-11 and 14-17 years have been identified at the sites of 800 m and 1560 m altitude respectively. The accumulation rate ranges between 150-170 kg m⁻² y⁻¹ and 150-180 kg m⁻² y⁻¹ at the first and the second of these two sites.

KEY WORDS: Snow, Firn cores, Ion chromatography, Chemical composition, Accumulation rate.

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RIASSUNTO: CAPRIOLI R., GRAGNANI R., GUGLIELMIN M., SMIRAGLIA C., PROPOSITO M. & TORCINI S., *Profili chimici da trincee di neve e carote di nevato superficiale per lo studio dei tassi di accumulo sul Ghiacciaio Campbell (Terra Vittoria Settentrionale, Antartide)*. (IT ISSN 0391-9838, 1997).

È stato effettuato lo studio della composizione chimica (Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, CH₃SO₃⁻ (Msa), Cl⁻, NO₃⁻, SO₄⁼⁼) in campioni di neve e firn prelevate in tre stazioni (A - 74°41' S-164°30' E; B - 74° 15' S-164°04' E e C - 73 45' S-163° 20' E) localizzate sul Campbell Glacier (Antartide) a diversa altitudine (50, 800 e 1560 m).

Nella stazione costiera il contributo di sali di origine marina è molto consistente soprattutto in coincidenza di forti mareggiate. Procedendo verso l'interno e con l'aumento della quota il contributo dello spray marino si attenua anche se permane ben riconoscibile anche al sito C.

Le differenze quantitative, tra le diverse specie chimiche, riscontrate nei campioni della stazione B e C sono da interpretare prendendo in considerazione sia le reazioni chimiche e i processi di frazionamento che intervengono quando masse d'aria di origine oceanica penetrano all'interno del continente, sia considerando masse d'aria di differente origine.

Le variazioni della concentrazione Msa, H₂O₂, nss SO₄⁼⁼, NO₃⁻ e nss Ca⁺⁺ mostrano marcati andamenti stagionali che permettono di stimare in 10-11 anni e in 14-17 anni l'età della parte più profonda delle carote prelevate rispettivamente nel sito B e C. La velocità di accumulo varia da 150-170 kg m⁻² y⁻¹ a 150-180 kg m⁻² y⁻¹ rispettivamente per il sito B e C.

TERMINI CHIAVE: Neve, Carote di firn, Cromatografia ionica, Composizione chimica, Velocità di accumulo.

INTRODUCTION

In the last few years there has been growing interest in the study of the polar ice-sheet and in the reconstruction of interrelationships between the chemistry of the atmosphere and the paleoclimate (Legrand & alii, 1988; Dansgaard & Oeschger, 1989; Khalil & Rasmussen, 1989). Moreover, studies on the Antarctic ice-sheet mass balance are very relevant to understanding the relationship between global warming and sea level change.

The chemical composition of snow and firn samples, from the Campbell Glacier (Northern Victoria Land), was

studied to investigate seasonal signal and the chemical contribution from some different emission sources (marine biogenic activity, sea and crustal). The new data on the snow accumulation rate of the Campbell Glacier will be useful to improve the evaluation of the mass balance of this glacier.

SAMPLING AND ANALYSIS

A snow pit (2 m in depth) 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, and 50 m a.s.l., during the 1994-95 Italian Antarctic Expedition. Another snow pit (1.4 m) was dug in the Campbell Glacier at about 800 m a.s.l. (site B, 74° 15' S-164°04' E), just opposite Mt. Campbell about 50 km from the frontal ice cliff. At the bottom of this pit a core (2.37 m) was collected. Finally, a core (7 m) was taken at the altitude of 1560 m from the upper sector of this glacier, not far from the confluence of the tributary Recoil Glacier and at about 110 km from the ice cliff (site C, 73° 45' S-163° 20' E). The sampling map is shown in fig. 1.

Site A, at the glacier tongue, is situated in the percolation zone, where surface melting occurs in summer; the pit

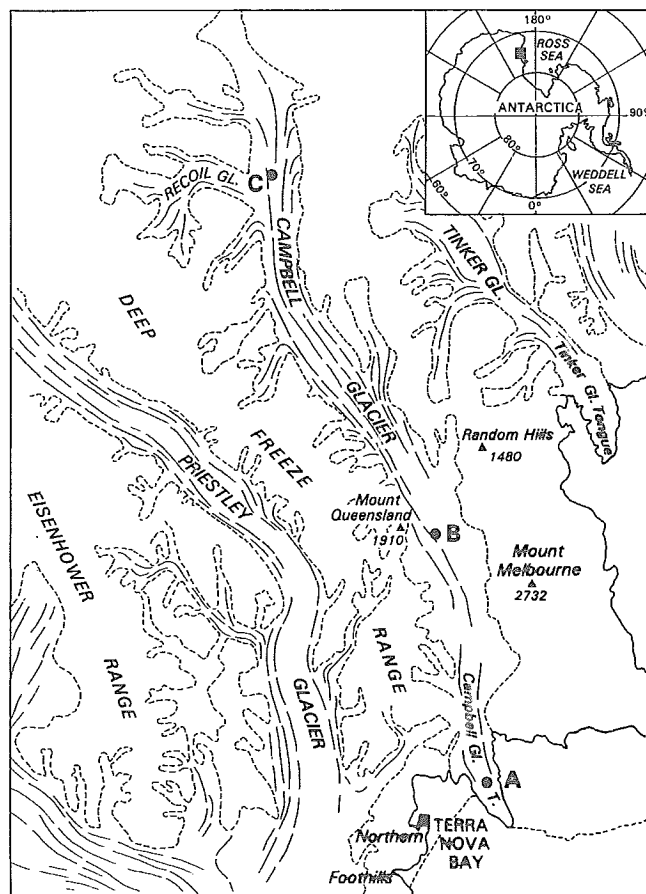


FIG. 1 - Location of sampling sites.

dug in this area revealed many ice layers and pipe-like structures such as ice glands. Sites B and C are located in the dry-snow zone of the Campbell Glacier, as demonstrated by the temperatures at a depth of 3.5 m, of well below -20 °C; no melting usually occurs here.

Samples were stored frozen. Then after surface cleaning in a cold room, they were sub-sampled and stored in pre-cleaned (by 18 Mohm ultra-pure-water) polyethylene containers and sent to the laboratory where they were melted in a clean room before chemical analyses.

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

Analyses of Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, CH₃SO₃⁻ (Msa), Cl⁻, NO₃⁻, SO₄⁼ were performed by ion chromatography (Dionex 2020i). Anion separation was obtained with a Dionex AS5 column (Legrand et al., 1993) and NaOH eluent. To begin with, in order to obtain a good separation of Msa from other organic compounds, a 5 10⁻⁴ N NaOH was used and, after 8 minutes the NaOH concentration was increased to 3 10⁻² N to elute the other inorganic ions within 14 minutes. NaOH free from CO₃⁼ (Baker) was diluted with 18 Mohm ultra-purewater in which dissolved gases were stripped by a helium flow. An anion trap column (Dionex, Ion Pac Atc-1) was placed on the eluent line to strip trace anionic contaminants. The eluent flow was 2 mL/min⁻¹ and the sample volume 3.5 mL. Cation separation was by Dionex CS12 (methane sulfonic acid 20 mM eluent). The eluent flow was 1 mL/min⁻¹ and the sample volume 1.5 mL.

H₂O₂ was analyzed by an electrochemical detector (Antec mod. «Decade») equipped with a micro flowcell (volume 0.005 µl) with a Pt working electrode (diameter 0.5 mm) in which the potential of the cell was 650 mV. The detector was in line with a pump and chromatograph injection valve. The flow rate of the mobile phase (0.01 M Na₂HPO₄-0.01 N KH₂PO₄ solution) was 0.4 mL/min⁻¹ and the loop 100 µL.

The relative repeatability, for all chemical species analyzed, was higher than 10%. For more detailed information on the repeatability of cations and anions see Caprioli & alii (1997), whereas statistical results for the repeated run of H₂O₂ are shown in tab. 1.

TABLE 1 - Repeatability of H₂O₂ standard solution determination.

H2O2 µg/L-1	n° of samples	Mean p. height nA (a. unit)	Std Dev.
20	4	166	3.5
40	4	307	13.3
80	12	531	43.1
160	5	1140	20

RESULTS AND DISCUSSION

Chemistry of firn

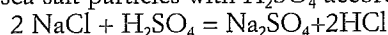
The mean concentration of analyzed ions is reported in tab. 2. The concentration of the elements derived from sea salt (typically Na, Mg and Cl) decreases rapidly from the

coast to the higher altitudes. This feature has already been described, at different Antarctic sites, by Delmas & *alii* (1985), Herron & Langway (1979), Minikin & *alii* (1994), Mulvaney & *alii* (1993) and, at Northern Victoria Land, by Piccardi & *alii* (1994 and 1996) and Caprioli & *alii* (1997).

The higher sea salt concentration encountered at the Campbell Glacier Tongue, about 6 km from the ice edge, is due mainly to dry deposition of large particles from sea salt aerosol during sea storms (fig. 2). This process has been observed e.g. at the Filcher-Ronne Ice Shelf (Minikin & *alii*, 1994). The event recorded in the firm layer at a depth of about 40 cm at site A could be attributed to the storm that at the beginning of June 1993 struck the Ross Ice Shelf and then moved toward the Transantarctic Mountains. The wind storm was so severe that some of the automatic weather stations on the Ross Ice Shelf suffered damage (Stearns & *alii*, 1994).

In the correlation between Na^+ and Cl^- the equation of the regression lines is $\text{Cl}^- \mu\text{Eq L}^{-1} = 2.016 + 0.986 \text{Na}^+ \mu\text{Eq L}^{-1}$ ($r = 0.992$, $n = 156$) for site C and $\text{Cl}^- \mu\text{Eq L}^{-1} = 6.014 + 1.067 \text{Na}^+ \mu\text{Eq L}^{-1}$ ($r = 0.977$, $n = 85$) for site B, which are close to the dilution line of bulk sea water ($\text{Cl}^-/\text{Na}^+ = 1.17$). This feature suggests, over the whole of the data set, the absence of significant fractionation of the reaction products (HCl and Na_2SO_4) between NaCl and H_2SO_4 (Legrand & Delmas, 1988). Nevertheless some samples show a Cl^-/Na^+ ratio significantly higher or lower than the Cl^-/Na^+ ratio in sea water.

At site A, the equation of the regression line is $\text{Cl}^- \mu\text{Eq L}^{-1} = 238.9 + 0.725 \text{Na}^+ \mu\text{Eq L}^{-1}$ ($r = 0.947$, $n = 21$) which indicates a Cl^-/Na^+ ratio significantly lower with respect to the sea water. This is due to an enrichment of Na_2SO_4 as shown from data in snow around 35 cm in depth. In the reaction of sea-salt particles with H_2SO_4 according to:



brings about the formation of a two different phases (gas and aerosol) that can be fractionated producing enrichment or depletion of Na_2SO_4 and HCl . Nevertheless, due to the high concentration of nss SO_4^{2-} post-deposition enrichment, by melt-refreezing, can be supposed.

The nss SO_4^{2-} ($\text{nss SO}_4^{2-} = \text{SO}_4^{2-} - 0.12 \text{Na}^+$, where all species are in $\mu\text{Eq L}^{-1}$) profile at site A is shown in fig. 2.

The mean $\text{Na}^+/\text{Mg}^{2+}$ ratios are 5.1, 4.4 and 5.4 for site A, B and C respectively, which are close to sea water $\text{Na}^+/\text{Mg}^{2+}$ ratio (4.14) according to Ikegami & *alii* (1994)

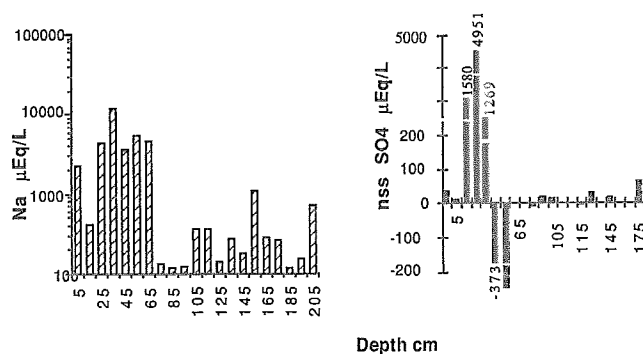


FIG. 2 - Na and nss SO4 profile at site A.

and McInnes & *alii* (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 a higher $\text{Na}^+/\text{Mg}^{2+}$ ratio, with respect to sea water, is observed suggesting sporadic depletion of Mg^{2+} relative to Na^+ . This is in agreement with Mulvaney & *alii*, (1993) as found studying fractionation of sea salt during transport across an Antarctic ice shelf.

Generally the Na^+/K^+ and $\text{Na}^+/\text{Ca}^{2+}$ ratios are much lower than the bulk sea water ratios at both site B and C. In fact percentages of the nss K^+ ($\text{nss K}^+ = \text{K}^+ - 0.0213 \text{Na}^+$, where all species are in $\mu\text{Eq L}^{-1}$) and the nss Ca^{2+} ($\text{nss Ca}^{2+} = \text{Ca}^{2+} - 0.043 \text{Na}^+$, where all species are in $\mu\text{Eq L}^{-1}$), with respect to the total content of these ions, are 72.8% and 81.8% at site B and 82.6% and 81.4% at site C. These percentages, which are close to the values found by Whitlow et. al. (1992) at the South Pole, confirm a prevailing crustal origin of K^+ and Ca^{2+} .

The Msa, produced in photo-oxidation of dimethylsulphide in turn derived from the biologically produced precursor dimethylsulfoniopropionate (Dacey & Blough, 1987), shows mean concentrations (0.21 μM) consistent with data obtained from other Antarctic sites (Ivey & *alii*, 1986; Minikin & *alii*, 1994; Legrand & *alii*, 1992; Mulvaney & *alii*, 1992; Prospero & *alii*, 1991; Saigne & Legrand, 1987). If the data of 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 with increasing altitude. In fact the mean concentration of Msa is 0.27 μM and 0.17 μM respectively at site B and C.

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

The mean concentrations of NO_3^- is 2.1 $\mu\text{Eq L}^{-1}$, 1.3 $\mu\text{Eq L}^{-1}$ and 0.97 $\mu\text{Eq L}^{-1}$ respectively at site A, B and C. These values are in agreement with the data at the other Antarctic sites (Caprioli & *alii*, 1997; Piccardi & *alii*, 1994; Legrand & Kichner, 1990; Neubauer & Heumann, 1988; Dahe & *alii*, 1992; Minikin & *alii*, 1994 and Whitlow & *alii*, 1992). Generally no simple relationship of concentration with altitude was found (Wolff, 1995) and the decreasing NO_3^- concentration vs altitude, observed here, could be due to different deposition rates of impurities at the three sites.

The contribution of sulphate in the Antarctic region is mainly due to marine biogenic activity and sea salt. Crustal and anthropic sources are generally negligible. Volcanic events can produce a significant input of SO_x in the atmosphere, which can increase SO_4 deposition and give a very well marked signal in the snow in sites either close to or far from eruptions (Hammer, 1977 and 1985, Delmas & *alii*, 1985, Moor & *alii*, 1991).

In our samples the mean $\text{nss SO}_4^{2-}/\text{SO}_4^{2-}$ ratio is -0.055, 0.54 and 0.42 at sites A, B and C respectively. Negative values of nss SO_4^{2-} can be found (especially in coastal polar si-

TABLE 2 - Analysis data of studied samples.

	Na ⁺ μEq L-1	K ⁺ μEq L-1	Mg ⁺⁺ μEq L-1	Ca ⁺⁺ μEq L-1	MSA μM	Cl ⁻ μEq L-1	NO ₃ ⁻ μEq L-1	SO ₄ ⁻ μEq L-1	nss SO ₄ ⁻ μEq L-1	H ₂ O ₂ μg L-1
CAMPBELL GLACIER TONGUE (50 m a.s.l.)										
Mean	1750	34	350	100	0.18	1570	2.1	564	354	31
Median	360	7.7	85	28	0.13	401	1.5	60	1.3	24
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.s.l.)										
Mean	39	4.9	8.9	10.2	0.27	48	1.3	11.4	6.7	8.4
Median	32	2.9	7.8	8.3	0.24	38	1.1	10	5.6	0.48
Std.Dev.	29	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.)										
Mean	21	3.7	3.7	4.1	0.17	22.8	0.97	3.8	1.3	8.5
Median	12	1.5	2.4	3.4	0.14	3.6	0.92	2.7	1.1	4.7
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

tes and in winter) due to not well known processes that lead to a lower SO₄⁻/Na⁺ ratio with respect to bulk sea water. The low nss SO₄⁻/SO₄⁻ ratio in site A confirms the strong marine influence that decreases quickly far from the sea. In site B the nss SO₄⁻/SO₄⁻ correlation is highly significant (r = 0.88, n = 85) whereas in site C the correlation is not so significant (r = 0.26, n = 156). Moreover the relationship between Ca⁺⁺, nss Ca⁺⁺, SO₄⁻ and nss SO₄⁻ at sites B and C is quite different. At site B a large part of the nss SO₄⁻ and nss Ca⁺⁺ could be as CaSO₄ while at site C nss SO₄⁻ and nss Ca⁺⁺ are not significantly correlated (fig. 3). Moreover nssCa⁺⁺/nss SO₄⁻ ratios (excluding negative values of nss SO₄⁻) are 1.41 and 3.73 respectively in site B and C due to a relative lower content of nss SO₄⁻ with re-

spect to other constituents in site C. This nss SO₄⁻ feature is spotted also by other ratios such as Msa/nss SO₄⁻ (0.092 and 0.26 at site B and C respectively).

H₂O₂ is produced in the atmosphere by photochemical processes which reach the maximum intensity during the summer period. Therefore atmosphere and snow show a peak in H₂O₂ concentration during this period. Because of this behaviour H₂O₂ is used as a seasonal tracer. The mean concentration of H₂O₂ is 8.45 μg L⁻¹ and 8.5 μg L⁻¹ respectively at site B and C. This suggests that there is no difference in deposition processes between these two sites.

The results of the Cluster analysis (amalgamation - single linkage; distance measure - 1 Pearson r) are shown in the dendrograms in figs. 4 and 5. They summarize some of the differences between samples collected at site B and C. In site B two clusters are well spotted, the first includes Na⁺, Cl⁻, K⁺, nss K⁺ and Mg⁺⁺, the second Ca⁺⁺, nss Ca⁺⁺,

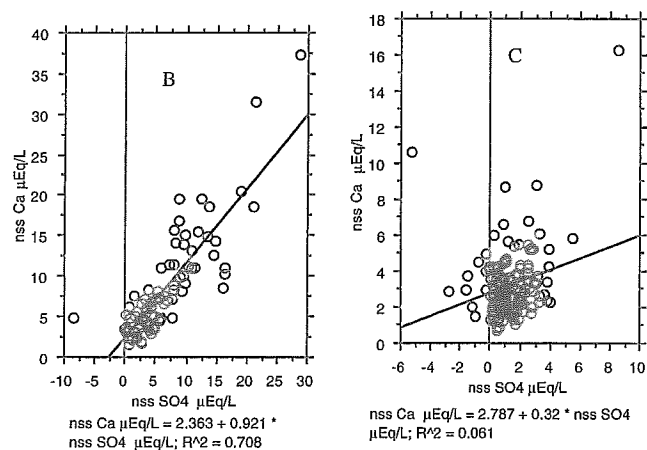


FIG. 3 - nss SO₄⁻ nss Ca correlation at sites B and C.

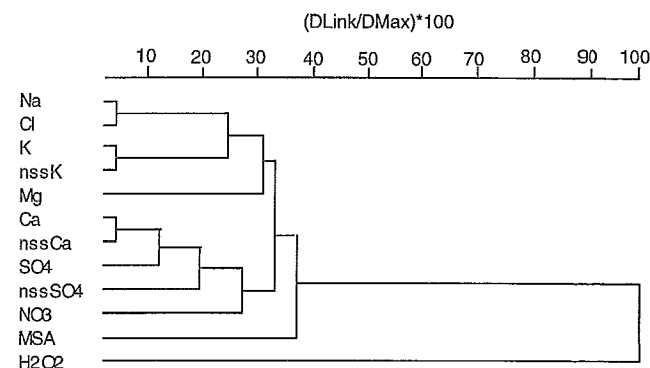


FIG. 4 - Dendrogram of chemical species at site B.

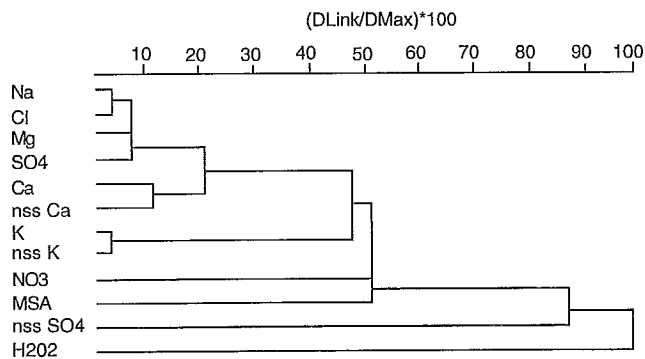


FIG. 5 - Dendrogram of chemical species at site C.

SO_4^- , nss SO_4^- and NO_3^- whereas Msa and H_2O_2 show a greater distance from these clusters. At site C a well defined cluster includes Na^+ , Cl^- , Mg^{++} , SO_4^- , Ca^{++} and nss Ca^{++} whereas K^+ , nss K^+ , NO_3^- , Msa, nss SO_4^- and H_2O_2 are at a greater distance.

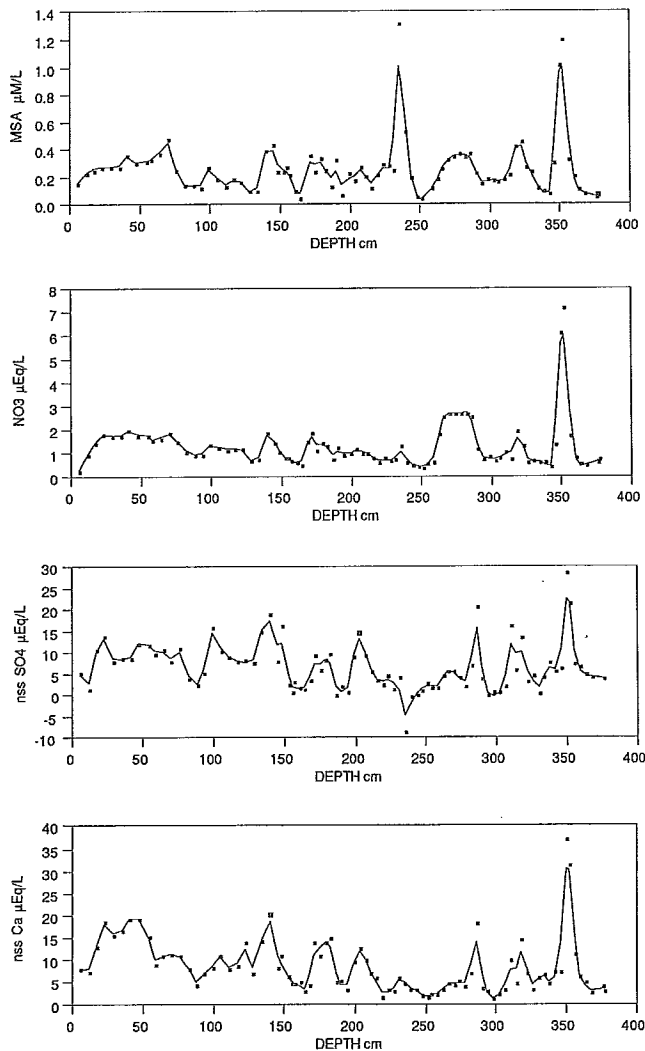


FIG. 6 - Profiles of chemical species at site B.

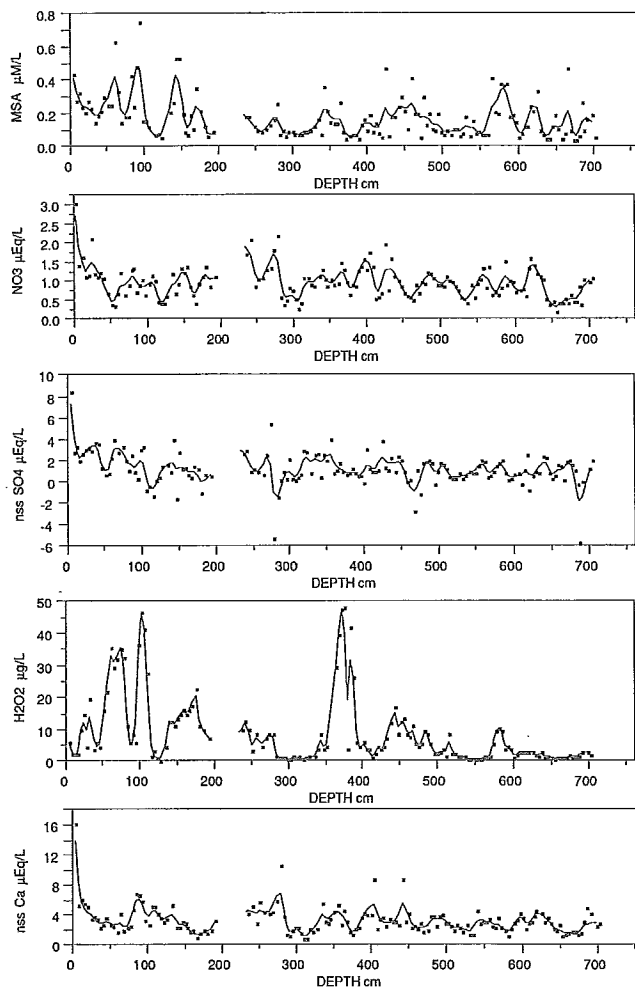


FIG. 7 - Profiles of chemical species at site C.

In order to explain the relationship between the elements and compounds studied in site C and B chemical fractionation and/or reaction inside air masses and of different origin from the air masses at the two sites can be considered. The peculiar chemical characteristics of firm at site B and C and in particular the sharp decrease in the nss SO_4^- cannot be explained by the fractionation of chemical species only and the contribution of masses of air of different origin have to be assumed at sites B and C.

Seasonal trend of chemical species

Figs. 6 and 7 show chemical profiles of H_2O_2 , Msa, nss SO_4^- , NO_3^- and nss Ca^{++} in site B and C. All species, if H_2O_2 in site B is not considered (due to the partial obliteration of the seasonal signal), show numerous fairly well preserved seasonal signals in which H_2O_2 , Msa, nss SO_4^- and NO_3^- peaks correspond to the late spring-summer period. Due to a significant correlation coefficient between nss Ca^{++} and NO_3^- ($r = 0.738$ and 0.62 at site B and C respectively), we suppose there to be nss Ca^{++} concentration maxima in late spring-early summer similar to NO_3^- .

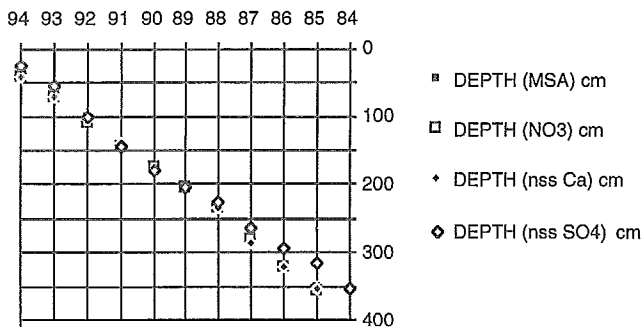


FIG. 8 - Chronological profile of different chemical species at site B.

Using chemical species profiles for dating snow layers, some of most important difficulties are related to the not very accurate overlapping between different profiles. To solve this problem Udisti (1996) suggests a method involving a sum of normalizing profiles. In the present paper we restrict data analysis plotting chemical species concentrations vs depth, fitting data by a cubic spline function (figs. 6 and 7) and then plotting depth, corresponding to different year for different chemical species, vs year (figs. 8 and 9). In this way the differences obtained by different chemical species profiles can be well spotted.

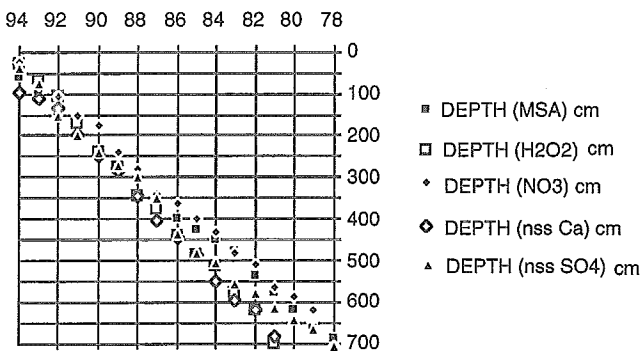


FIG. 9 - Chronological profile of different chemical species at site C.

At site B, 10-11 summer peaks have been identified according to Msa, NO_3^- , nss Ca^{++} or nss SO_4^- profiles respectively. At site C, 14-17 summer peaks have been identified according to nss Ca^{++} , H_2O_2 or Msa, NO_3^- profiles respectively.

The density profiles at site B and C are shown in fig. 10. The density values increase fairly well with depth and they are higher at site B than at site C. Taking into account the mean density (site B = 0.494, site C = 0.384) the accumulation rate is in the range of $150\text{-}170 \text{ kg m}^{-2} \text{ y}^{-1}$ at the altitude of 800 m a. s. l. and in the range of $150\text{-}180 \text{ kg m}^{-2} \text{ y}^{-1}$ at the altitude of 1560 m a.s.l.. These values are in agreement with those found by Udisti (1996) in the area of Terra Nova Bay while Zanoni, on the basis of glaciological considerations, proposed an accumulation rate of $200 \text{ kg m}^{-2} \text{ y}^{-1}$ at the Campbell Glacier Tongue.

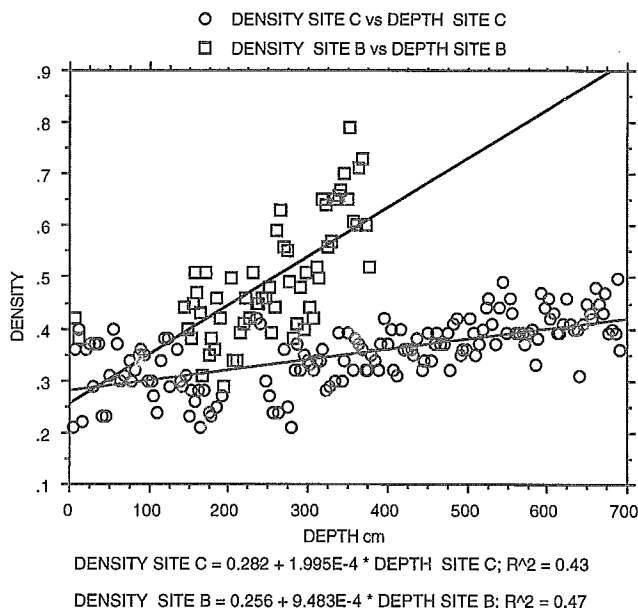


FIG. 10 - Correlation diagram of density vs depth at sites B and C.

CONCLUSION

The chemical composition of snow and firn samples from Campbell Glacier confirms the decrease of sea salt concentration with increasing altitude and distance from the sea. The mean concentration of Na^+ , for instance, falls from $1750 \mu\text{Eq L}^{-1}$ in the site A (with a maximum of $11930 \mu\text{Eq L}^{-1}$, an unusually high level, probably due to a strong sea storm) to 39 and $21 \mu\text{Eq L}^{-1}$ in site B and C respectively, where the maximum values exceed $210 \mu\text{Eq L}^{-1}$ by only a little.

The concentration of many of the elements and compounds studied (particularly H_2O_2 , Msa, nss SO_4^- , NO_3^- and nss Ca^{++}), offers a good seasonal signal, showing higher contents during late spring-summer periods. It is therefore possible to identify many annual cycles (14-17 for the longest firn core). Using the measured density values, the accumulation rate was also calculated for the lower and upper Campbell Glacier. It does not appear very different in both sites ($150\text{-}180 \text{ kg m}^{-2} \text{ y}^{-1}$) and agrees with the rates previously calculated in the same area. The results of further analyses involving stable isotope measurements will provide more clues to the temporal variation in snow accumulation.

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