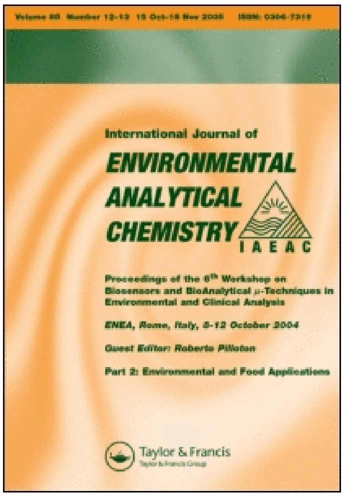

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NON-SEA-SALT CONTRIBUTION OF SOME CHEMICAL SPECIES TO THE SNOW COMPOSITION AT TERRA NOVA BAY (ANTARCTICA)

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The concentrations of main components of two series of snow samples collected in the area of Terra Nova Bay have been determined. From statistical analysis of the obtained values, Na, Cl and Mg result from marine contribution, whereas a constant excess of K and of Ca is added to the sea spray content of snow. A further source of sulfates, besides the ones produced in DMS oxidation, is evidenced in the $nssSO_4$ contribution. A good correlation among $nssSO_4$, MSA and NO_3 or nssCa is also observed.

KEY WORDS: Snow analysis, Antarctica, snow chemical composition, main components

INTRODUCTION

The interest of studying snow composition with depth of coastal areas of Antarctica is due to two principal reasons. First, the relatively high quantity of precipitation allows to distinguish the characteristics of single events, and second the proximity to sea facilitates the bio-geochemical investigation of aerosol particles and their deposition and conservation into the snow. The principal components analysis is also useful in the attempt to individualize different sources of snow constituents. The concentration of a single component is usually divided in two contributions: sea-salt and non sea-salt. The Na and Cl concentrations can be used to obtain the marine contribution of other components assuming that Na and Cl are exclusively of marine origin and that the sea spray is of the same composition of subsurface sea-water. Some authors used concentrations of elements of crustal[1,2] or cosmic origin[3] with the attempt to give a more complete interpretation to the non marine snow contributions. Contributions of sources different from sea salt, indicated as nss or ex, are frequently evidenced from enrichment factor (E.F.) calculations obtained as:

$$E.F. = ([X]/[Na])_{snow}/([X]/[Na])_{sea}$$

Table 1 shows some E.F. values obtained from the literature and usually calculated from mean concentration values and those we recalculated from the mean concentration of different papers using the above cited formula.

Table 1 Enrichment factors (E.F.) of Mg, K and Ca in snow samples of Antarctica.

Site	*Latitude*	*Longitude*	*alt/m*	*dist/Km*	*EF/Mg*	*EF/K*	*EF/Ca*	*ref*
Byrd station	79°59'S	120°01'W	1530	700	1.08	1.34	–	4
Mirny	66°33'S	93°01'E	820	45	1.23	1.22	–	5
Little America	78°10'S	162°13'W	0	0	1.08	1.79	–	6
Ross Ice Shelf C7	78°58'S	176°00'W	0	70	0.94	1.13	–	7
Ross Ice Shelf Base Camp	82°28'S	166°00'W	0	450	1.19	1.13	–	7
Ross Ice Shelf site E, F, G	–	–	–	650	1.48	3.94	–	7
Dome C	74°42'S	124°04'E	3240	910	1.24	1.69	1.69	8
Dome C	74°42'S	124°04'E	3240	910	1.04	2.10	1.73	9
Dome C	74°42'S	124°04'E	3240	910	1.10	2.05	1.64	10
James Ross Island Na > 0.25 mg/kg	64°13'S	57°38'W	1660	24	–	0.83	1.11	1
James Ross Island Na < 0.25 mg/kg	64°13'S	57°38'W	1660	24	–	3.73	5.35	1
South Pole	90°S	–	2880	1270	1.20	2.75	2.47	11
Vostok	78°28'S	106°48'E	3488	1300	–	1.88	–	2
South Pole	90°S	–	2880	1270	–	2.11	–	12
Riiser Larsenisen ice shelf	72°30'S	15°00'W	–	1	1.16	–	1.10	13
Riiser Larsenisen ice shelf	72°30'S	15°00'W	–	60	1.28	–	1.34	13
Riiser Larsenisen ice shelf	72°30'S	15°00'W	–	120	1.11	–	1.41	13
Byrd Station (0–1000 m)	79°59'S	120°01'W	1530	700	1.11	2.78	–	14
Crescent Scarp (peninsula)	69°42'S	66°25'W	1500	90	–	0.95	0.98	15
Law Dome	66°30'S	113°00'E	–	115	0.77	–	–	16
Vostok (0–325 m)	78°28'S	106°48'E	3488	1300	1.03	1.56	1.90	17
South Pole (1959–69)	90°S	–	2880	1270	–	2.11	–	18
South Pole (last 1000 y)	90°S	–	2880	1270	–	1.89	–	18
Dome C (238–360 m)	74°42'S	124°04'E	3240	910	–	1.06	–	19
Dome C (360–454 m)	74°42'S	124°04'E	3240	910	0.99	0.89	–	19
Dumont D'Urville	66°42'S	140°00'E	41	–	1.05	1.29	1.01	20
South Pole (1955–88)	90°S	–	2880	1270	2.10	2.75	9.98	21
Byrd Station	79°59'S	120°01'W	1530	700	1.17	–	–	22
Mc Carthy Ridge	74°32'S	162°56'E	700	40	0.95	1.86	2.16	–
Styx Glacier	73°51'S	163°41'E	1700	50	0.94	1.63	2.95	

The purpose of this paper is to discuss the non-sea spray effects on two series of snow samples obtained from pits opened in Northern Victoria Land (Antarctica).

EXPERIMENTAL

Sampling and analysis

In mid December 1990 two snow pits, 2 m deep, were dug at Styx Glacier (1700 m a.s.l., and 50 Km distance from the sea) and at Mc Carthy Ridge (700 m a.s.l., 40 Km distance from the sea). Two series of progressively numbered vials, one 16 × 100 mm and another 35 × 100 mm, were inserted in the walls of each pit. The small diameter vials were divided into even and odd numbers. The snow of the even numbered vials were analysed for H_2O_2 while the odd ones for only anions. The results of these analysis have already been reported[23]. The snow of the large diameter vials was analysed for H_2O_2, anions and cations. These analysis provide a more complete characterization of a single snow layer.

The hydrogen peroxide was determined by flow analysis using p-hydroxyphenylacetic acid and peroxidase and fluorescence intensity measurement.

Anions were determined by Ion-chromatography using a Dionex AS5A column for fluorides and organic acids (acetic, formic and methanesulphonic (MSA)) and a Dionex AS4A for inorganic anions. The eluents used were, respectively, 3.3 mM borax and 1.2 mM $NaHCO_3$ + 1.3 mM Na_2CO_3.[24] The instrument was equipped with a conductivity detector with suppression.

Cations were determined by ion chromatography using a Dionex CS10 column, eluted with 20 mM HCl + 0.5 mM diaminopropionic acid[24] and a conductivity detector with suppression.

Samples were introduced into the chromatograph immediately after melting and filtration on 0.45 μm membrane so to avoid eluent effects on eventually present suspended solid matter. In fact, as described by De Angelis *et al.*[2], only the Na of marine origin is present in the melting. The Na of alluminosilicates is completely solubilized passing through the chromatographic column[25]. In absence of a preliminary filtration, Na of marine origin was recognised from crustal Na measuring the Al content and considering the ratio of mean concentrations in the earth crust[26].

Further indications on the sampling mode and laboratory activity have been described elsewhere[23].

RESULTS AND DISCUSSION

As previously observed[23], the H_2O_2 concentration show a cyclic behaviour with spring maximum, which allows the recovery of annual layers. The H_2O_2 concentration as a function of samples depth for both pit are reported in the continuos curve of Figure 1. The depositions in the Styx Glacier pit, dated according to the H_2O_2 records, correspond to the period 1986–1990, with a mean resolution of 10 samples per year. On the other hand, the Mc Carthy Ridge pit covers the period 1987–1990 with a mean resolution of 15 samples per year. This dating is confirmed by a plot obtained from the cross comparison of the concentration of H_2O_2, $nssSO_4$, and MSA[27]. A plot of Cl/Na versus depth confirms the time series for Styx Glacier, whereas, for the lower sampling place, the identification of the time series is not possible, as the curve does not show a well defined trend.

The Na concentration profiles (bar histograms in Figure 1), show very high values primarily in winter samples. Profiles obtained for different ions which are the main constituents of sea water (i.e. Cl, Mg, Ca, K and total sulfate), evidence high values of concentration at the same depth. Besides, considering for these elements the concentration ratio X/Na with increasing Na concentrations, the data points follow the line relative to the X/Na ratio of sea water. Assuming that the samples with high Na content have been deposited during salt storms, it is evident that the samples collected must be treated differently, and two groups with high Na content (H-Na) and low Na content (L-Na) must be determined for each pit. The frequency histograms of Na concentration of both sampling places were constructed in order to identify the threshold between the two groups of samples. The analysis of distribution show that most samples (78% and 83% for Styx Glacier and Mc Carthy Ridge, respectively) are grouped in contiguous classes of frequency in the range of low Na concentrations. The least samples are distributed in frequency classes well separated from the previous samples in the range of high Na concentrations. On the basis of these considerations, the threshold limits were established to be 0.25 and 1.0 mg Na/Kg for Styx Glacier and Mc Carthy

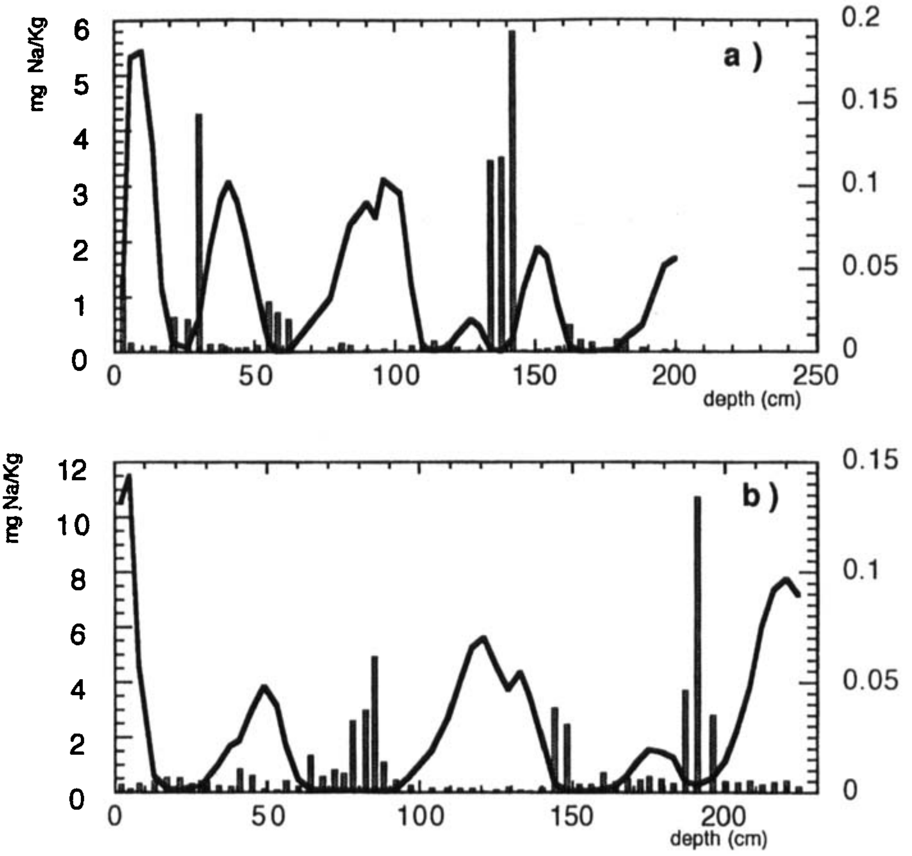

Figure 1 Time series of H_2O_2 (line) and Na (bars) in a) Styx Glacier, b) Mc Carthy Ridge samples.

Ridge, respectively. The same threshold limits were obtained in the analysis of clusters of the Euclidean distances among samples in space defined by the Na, Cl, Mg, Ca, K, and sulfates variables[28].

A further classification was introduced, on the basis of H_2O_2 concentration, to follow the time series of layer sequences. A biased value of 10 μg H_2O_2/Kg was used to distinguish the summer from winter samples. A so small value for H_2O_2 concentration was chosen to include the small maximum relative to the Antarctic summer of 1987–1988. This annual cycle, whose existence could be questioned on the basis of the H_2O_2 profile only (Figure 1), is in fact confirmed by the other measures considered for dating (nss-SO_4, MSA, and Cl/Na). After this classification, the samples of the H-Na group are all winter samples for the Mc Carthy Ridge sampling place, whereas in the Styx Glacier, two summer samples are present. Winter and summer samples are present in the L-Na group for both sampling places, with a prevailing presence of summer samples.

Once the possibility to separate the samples in three groups has been established (L-Na/s = summer, L-Na/w and H-Na/w = winter), the H-Na/s practically does not exist. The mean concentration of Na, Mg, K, Ca and sulfates for each group was calculated and, from these data, the E.F. were obtained with respect to Na (Table 2). It can be noted that the E.F. increases from H-Na/w to L-Na/s and that Cl and Mg have a different behaviour from K and Ca. For the first two ions small variations of E.F. are observed (values around 1), very close to the sea salt ratio. On the contrary, for K and Ca, large variations of E.F. are observed, reaching the value of 15 for Ca at Styx Glacier. In Table 2 (last column) is also reported the value of mean Na concentration used for calculating the single E.F. values; this allows to observe an inverse relationship between E.F relative to K and to Ca and the mean Na concentrations. This fact could lead to hypothesise a constant contribution to E.F. of nssK and nssCa which became less important as the contribution of sea K and Ca increases.

The values of E.F. obtained from our measurements as a mean of all samples of each sampling place are also reported in Table 1. As we can see, the value of E.F for Mg is about 1, whereas those of K and Ca are about the double. Therefore, the E.F. calculated from the mean of all samples, as usually reported, bring only a modest contribution to the knowledge of the phenomenon.

On the other hand, as indicated in Table 1, different authors report values always close to 1 for E.F. relative to Mg and values often greater than 1 for K and Ca, indicating that also in different regions of Anctartica it exists a different behaviour of Mg, primarily of marine origin, in comparison to K and Ca, which would have other origin in addition to sea salt contribution. An example of separation based on Na content has been attempted by Aristarain *et al.*[1] who separated the samples collected at Ross Island in two series. The E.F. values of K and Ca at L-Na resulted higher than those of H-Na. Analogous conclusions were drown by Warburton *et al.*[29] from the analysis of Ross Ice Shelf snow. Tuncel *et al.*[3] separated aerosol samples collected at Amundsen-Scott base on seasonal basis. The E.F. values of Mg, K and Ca, calculated for winter samples resulted 1.23, 1.56 and 1.53, respectively, whereas, for the summer samples, values of 1.53, 2.58, and 3.03 were found. The contribution of the marine source to the different variables was investigated, through the analysis of linear regression versus Na used as tracer of the sea-salt source, on groups separated for each sampling place (four plots = 2 sampling places × 2 groups, H-Na and L-Na). Each plot reports the value of the ratio corresponding to bulk sea water (dashed line) and the regression line (continuous line) when the model significance is greater than 99%. As it concerns the H-Na samples relative to Styx Glacier, the only two summer samples show a behaviour very different from that of the winter samples. For this reason the regression lines relative to H-Na are all calculated on winter samples.

Table 2 Enrichment factors (E.F.) of Cl, Mg, K, Ca and sulfates in samples of Styx Glacier and Mc Carthy Ridge.

		Cl	*Mg*	*K*	*Ca*	*SO_4*	*Mean Na concentration mg/Kg*
Styx Glacier	H-Na/w	0.87	0.80	1.20	1.49	0.93	1.858
	L-Na/w	0.97	0.83	3.43	5.58	1.23	0.178
	L-Na/s	1.18	1.07	4.22	15.31	3.85	0.077
Mc Carthy Ridge	H-Na/w	1.03	0.88	1.13	1.33	1.04	3.588
	L-Na/w	0.93	0.90	3.11	3.49	1.55	0.471
	L-Na/s	1.00	0.90	3.58	4.18	2.79	0.295

Chlorides

For the H-Na samples in both sampling places a good correlation between Cl and Na was observed (Figures 2a and 2c). The regression of Cl over Na, relative to the sea salt (theoretical regression) is basically coincident to the regression calculated for the samples of the lower station, whereas, for the higher station, the data points are mostly lower than that of the sea salt. For the L-Na samples of the Styx Glacier (Figure 2b) the sample regression crosses the theoretical regression near the value of 0.14 mg Na/Kg, because the samples with a higher Na concentration, mostly winter samples, have Cl concentrations lower than that of the sea salt. On the contrary the summer samples, characterised by lower Na content, show a Cl/Na ratio higher than the sea salt. For this reason the Cl/Na ratio can give a valuable indication of the season alternance. In the

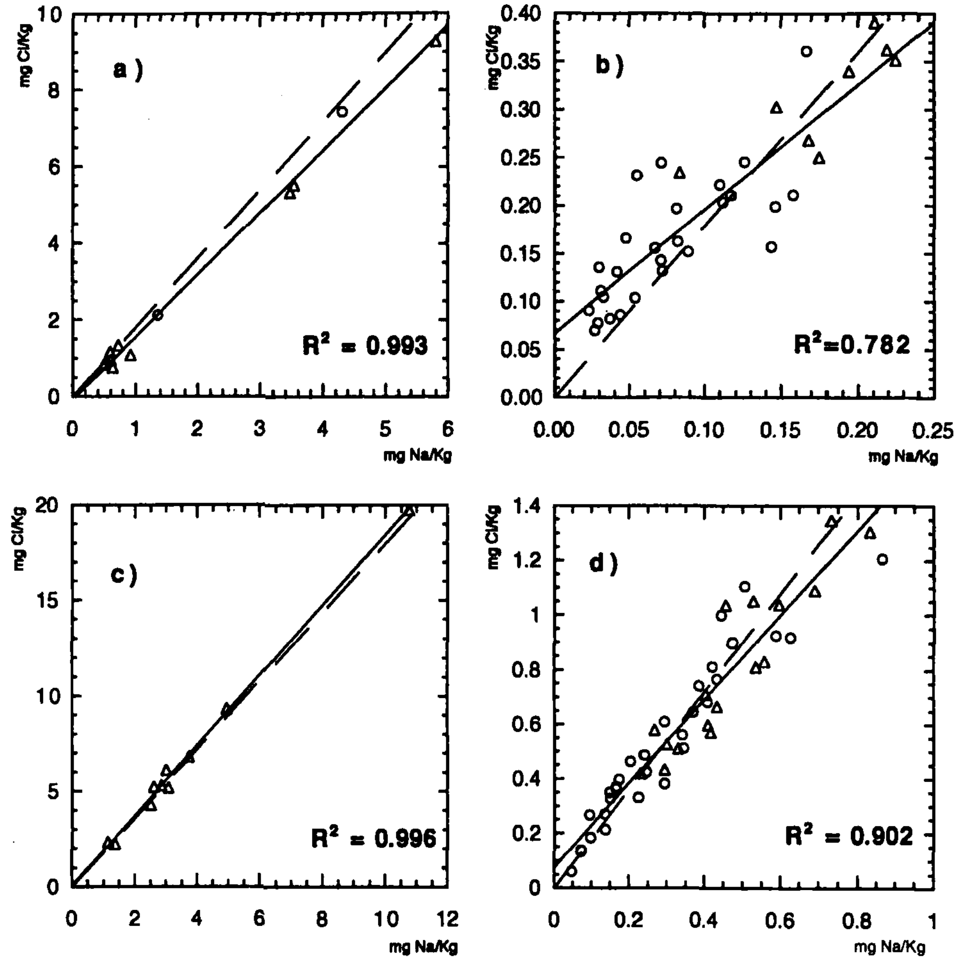

Figure 2 Plot of Cl concentration versus Na concentration; a) and b) Styx Glacier, c) and d) Mc Carthy Ridge; a) and c) H-Na, b) and d) L-Na; o summer samples, Δ winter samples; ——— regression line, — — sea water composition.

lower station (Figure 2d) the phenomenon occur with weaker intensity and the Cl/Na ratio is not reliable marker of season alternance. Legrand and Delmas[19] noticed that the Cl/Na ratio is generally very close to that of bulk sea water near the coast and begins to increase at the edge of the Antarctic plateau. Inasmuch, this ratio has seasonal variations with evident summer maxima at South Pole[12,21].

Magnesium

The magnesium ion show a behaviour similar to that of Cl (Figure 3). The H-Na samples of the higher station are primarily depleted of Mg. Only the two summer samples have different behaviour in comparison to the winter samples. As for L-Na samples, the regression line, always significative, intercept the theoretical regression, as the winter

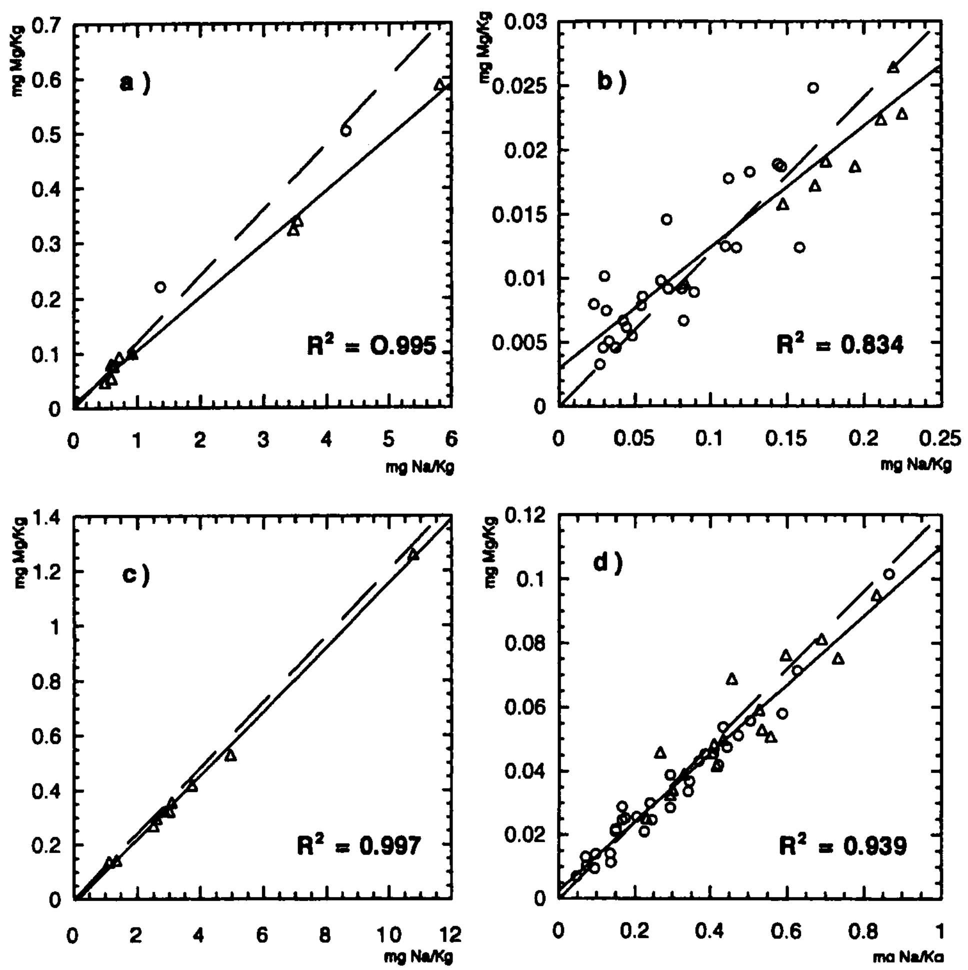

Figure 3 Plot of Mg, concentration versus Na concentration; a) and b) Styx Glacier, c) and d) Mc Carthy Ridge; a) and c) H-Na, b) and d) L-Na; o summer samples, Δ winter samples; ——— regression line, — — sea water composition.

samples are lower in Mg and summer samples are primarily enriched. Also for this element it is possible to establish a seasonal alternance from the Mg/Na ratio.

The samples from Mc Carthy Ridge, i.e. the lower station (Figure 3c), are practically aligned to the theoretical regression. The modest deviation of the values of Cl and Mg concentration from the theoretical regression evidences that, for this station, the fractionating process is only partially active, and that the transport processes remain conservative in the areas along the coast. The good correlation between Mg and Cl ($R^2 = 0.925$) found by Mulvaney *et al.*[30] in samples from Filibusen, lead the authors to hypothesise that the two species were related in the aerosol even as $MgCl_2$. A non negligible percentage (5%) of $MgCl_2$ particles was observed by Artaxo *et al.*[31] in an aerosol of Brazilian Antarctic Station at King George Island.

The use of sodium as an indicator of marine contribution seems to be justified, in this case, by the good correlation of Cl and Mg with Na (Figures 2 and 3) and of Cl with Mg (Styx Glacier $R^2 = 0.73$, Mc Carthy Ridge $R^2 = 0.89$), which lead to hypothesise that all three elements have the same origin, being in the same ratio as in sea salt. The plots of Figures 2 and 3 confirm the data in Table 2 where the E.F relative to Cl and Mg are close to 1. As indicated in Table 1, where the E.F. values are, also in this case, close to unity, the phenomenon is not restricted to our sampling area confirming, unlike K and Ca, the marine origin of Mg. The concentration of Mg in South Pole aerosol is controlled by marine aerosol all year along[3]. The lack of a crustal contribution for Mg is revealed not only in the soluble component of the snow melt, but also in the suspended solid fraction. The data of Boutron[9-11,32] relative to samples collected at Dome C and in South Pole, performed after a solubilization of aluminosilicates with HF, show, also in this case, the lack of a Mg excess with respect to marine Mg.

Potassium

In samples classified as H-Na of both sampling places (Figures 4a and 4c) a very good linear regression between K and Na is observed and the slopes are similar to that of the sea salt as the regression lines are parallel to the theoretical regression. The intercepts of these lines are significative, different from zero, and corresponding to 16 and 10 µg K/Kg for Styx Glacier and Mc Carthy Ridge, respectively. In the higher station one of the two samples classified as summer samples shows a K/Na ratio much greater with respect to that of winter samples (Figure 4a). The L-Na samples of Mc Carthy Ridge (Figure 4d) show again a parallelism with the theoretical regression albeit with a low regression coefficient. In this case also all the samples are richer in K and the intercept indicate a contribution of about 20 µg K/Kg. For the higher station it is not possible to establish any regression (Figure 4b) and all samples have a K concentration higher than the sea salt and the median is about 11 µg/kg. Therefore, a constant background contribution exists for K in both station, that is independent of marine contribution.

Calcium

Calcium behaves mostly like potassium. For this element also the winter samples of the H-Na group of both sampling station lies on lines parallel to the theoretical regression with a significative intercept of 40 µg Ca/Kg for both stations (Figures 5a and 5c). As observed for Mg at Styx Glacier, both samples classified as summer samples have higher Ca concentration in comparison with the corresponding winter samples (Figure 5a).

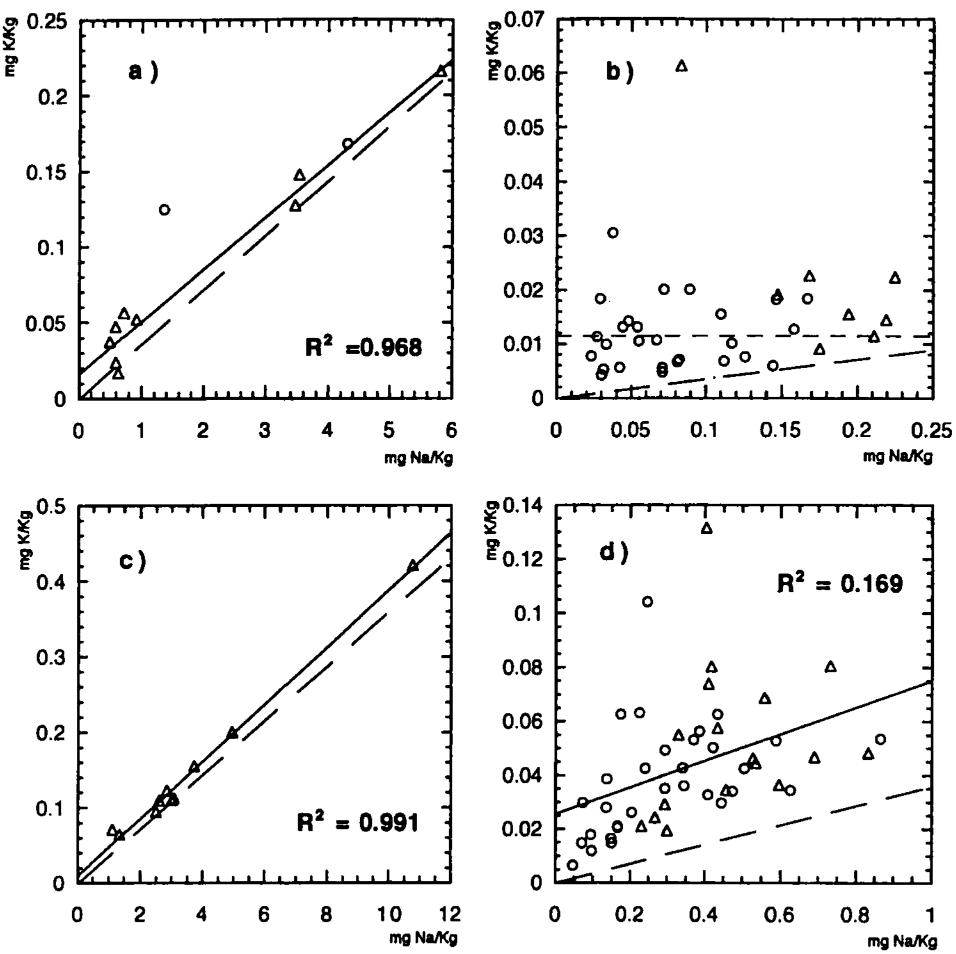

Figure 4 Plot of K concentration versus Na concentration; a) and b) Styx Glacier, c) and d) Mc Carthy Ridge; a) and c) H-Na, b) and d) L-Na; o summer samples, Δ winter samples; ——— regression line, — — sea water composition, - - - - median concentration.

All the L-Na samples (Figures 5b and 5d) show a Ca excess in comparison with the sea salt contribution and, also in this case, the L-Na samples of Styx Glacier have a median concentration similar to that revealed by the intercept of the H-Na samples. The K/Na and Ca/Na time series do not evidence any appreciable seasonal trend, as the background noise is high. On the other hand, the median values of the L-Na samples are comparable both for Ca and K with the values of the intercept of the H-Na samples, suggesting that the contribution of marine spray is added to contributions of different origin, homogeneously distributed and particularly evident when the weather conditions do not facilitate the sea salt input.

A different behaviour between Mg from one side, and Ca and K from the other is evidenced in Table 2. The same difference has been evidenced in different regions of Antarctica as reported in Table 1. The presence of an excess of Ca and K

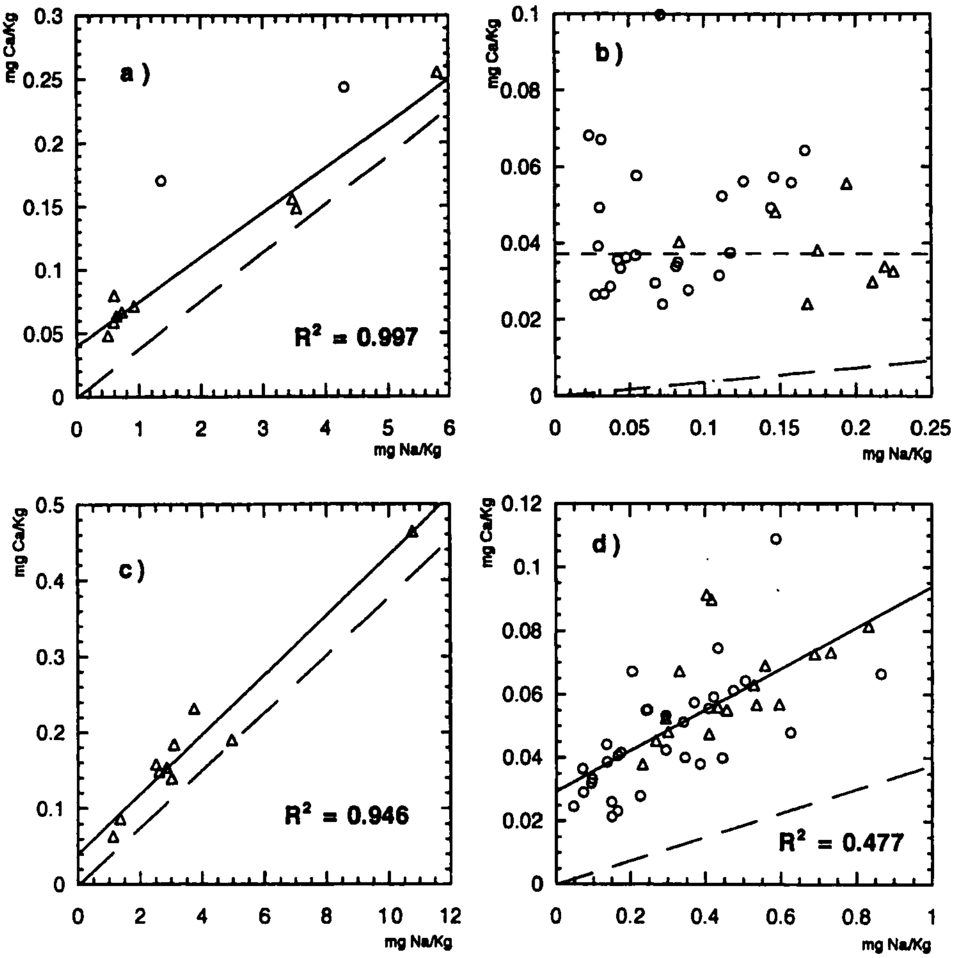

Figure 5 Plot of Ca concentration versus Na concentration; a) and b) Styx Glacier, c) and d) Mc Carthy Ridge; a) and c) H-Na, b) and d) L-Na; o summer samples, Δ winter samples; ——— regression line, — — sea water composition, - - - - median concentration.

contents compared to sea salt (Na and Mg) has also been found in aerosols of South Pole[3,33], Syowa Station[34], King Geoge Island, Antarctic Peninsula[31] and East Antarctic Plateau[35].

The Ca excess is ascribed to a contribution of crustal[13] or marine biogenic (coccoliths)[36] $CaCO_3$. The lack of carbonates in ice observed by Legrand *et al.*[37] lead to hypothesise that the nssCa is linked with both $nssSO_4$ and NO_3, the presence of $CaSO_4$ cristals in Antarctic aerosol has been evidenced by scanning electron microscopy and PIXE[31,36]. Also for K the crustal origin has been proposed[7]. A few authors support the idea that the excess of various substances in aerosols is the result of a chemical fractionation during the production of atmospheric sea salt particles by bursting bubbles[38,39].

Sulfates

The regressions between sulfate and sodium, for the H-Na group, are similar to those of Cl and Mg (Figures 6a and c). The correlation coefficients are high and the slopes close to those of the theoretical regression and for these samples, essentially winter samples, the marine spray is the main source of sulfates. Also in this case the two summer samples of Styx Glacier have a different behaviour compared with the winter samples (Figure 6a).

On the contrary for the L-Na group (Figures 6b and 6d), in which prevalently summer samples are included, the behaviour is similar to that of K and Ca. The low significance of the correlations over Na (95% probability level) and concentrations higher than the sea salt ratio indicate a contribution of different origin.

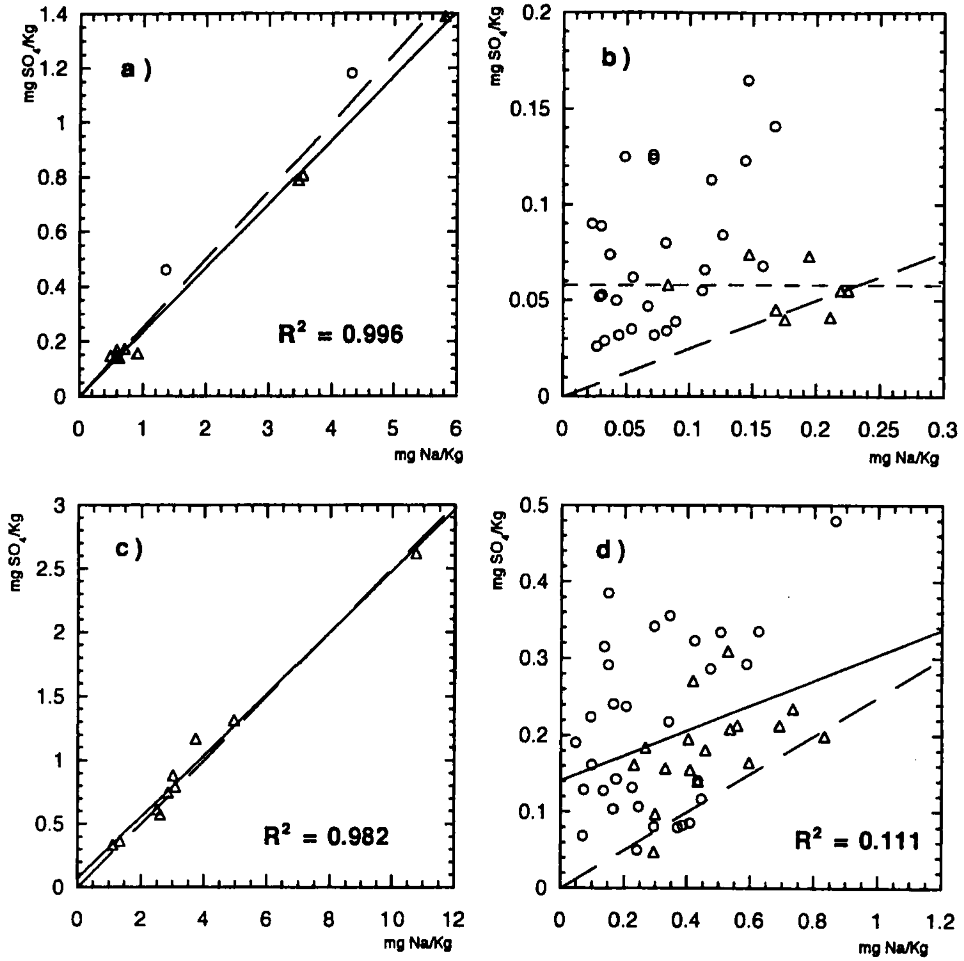

Figure 6 Plot of SO_4^{2-} concentration versus Na concentration; a) and b) Styx Glacier, c) and d) Mc Carthy Ridge; a) and c) H-Na, b) and d) L-Na; o summer samples, Δ winter samples; ——— regression line, — — sea water composition, - - - - median concentration.

From the median concentration values used for Table 2 it is possible to estimate that, in L-Na/s samples, 26% of the Styx Glacier and 36% of the Mc Carthy Ridge sulfates are of sea origin. For both stations this value is 100 % in H-Na/w samples.

The decrease of the marine contribution with the distance from the coast has been evidenced by Mulvaney *et al.*[30] determining the concentrations of Na and sulfates along a transect of the Fimbul Ice Shelf in Dronning Maud Land. Marine sulfates of shallow samples collected during January 1990 have a mean value of 20% of the total sulfates. This percentage changes along the transect from 45% near the coast to 10% at 120 Km of distance from the sea[30]. Previous papers evidenced that variations in the chemistry of snow are not a simple function of distance from the sea[7] but that the critical parameter for the transport of bulk sea-salt aerosol is elevation rather than distance from the coast[40]. This reduction of percentage of marine sulfates may be ascribed to the slow oxidation of SO_2, but also to a possible contribution of $nssSO_4$ from long range sources, or to a shorter residence time of the sea-salt particles[30]. Whitlow *et al.*[21] found that the marine contribution is only 5% at the South Pole.

In the southern hemisphere the biogenic source of sulphur became prevalent because the anthropogenic contribution is practically negligible[41]. In fact, considering the analogies between the time series of sulfates of the two stations[23], the source of $nssSO_4$ may be supposed to be the biogenic sulfate produced in the oxidation of dimethylsulfide (DMS). Strong covariations of MSA and $nssSO_4$, determined in aerosols, have been observed in several remote marine stations[42,43], but evident seasonal cycles are found above all in high latitude stations: Shemya Island (52°N)[42], Cape Grim (40°S), where a good relation was found among DMS, MSA and $nssSO_4$ determined in the atmosphere[44–46], Amsterdam Island (38°S)[47] and Mawson, East Antarctica (67°S)[48]. The good correlation among the above mentioned components strongly indicates their common source.

The sulphur cycle in the ocean-atmosphere system is influenced by climatic variability and produces changes in the $nssSO_4$/MSA concentration ratio.

In addition to the temperature effect on branching ratio of the oxidation of DMS (this effect was observed in laboratory experiments by Hynes[49] and supported by Berresheim[50] to explain the variation of the MSA/$nssSO_4$ ratio with latitude, even if the phenomenon was not always observed[44,48]), the wind velocity plays an important role both on oceanic emissions of air/sea exchanging rates[51] and on the abundance of sulfur dioxide and fine particle sulfate aerosols and the resulting size distribution of the marine aerosols[52].

A preliminary evaluation of errors associated with the determination of nss-SO_4 concentrations is necessary to usefully utilise these values. In fact, as the analytical error associated with the direct determination of Na and SO_4 is less than 5%, (3% using our methodology[24]), it is necessary to remember that the concentration of $nssSO_4$ results from the difference of two concentration values. Therefore, a calculation procedure[53] has been applied for the relative analytical precision, and the discussion is restricted only to values with a relative error less than 10%. So, all H-Na samples and most of the L-Na/w were discarded, and the drawn conclusions may be considered as valid for summer samples only.

The plots reported in Figure 7 were constructed using these data to evaluate the contribution of $nssSO_4$ (possibly of different origin) in comparison with the MSA concentration (of sole biogenic origin).

For the Mc Carthy Ridge samples (Figure 7b), a good linear relation was found between $nssSO_4$ and MSA concentrations following the equation:

$[nssSO_4] = 1.89\ [MSA] + 50.8$; $N = 25$, $R^2 = 0.75$
std. error 0.23 16.4
sig. level 0.000 0.005

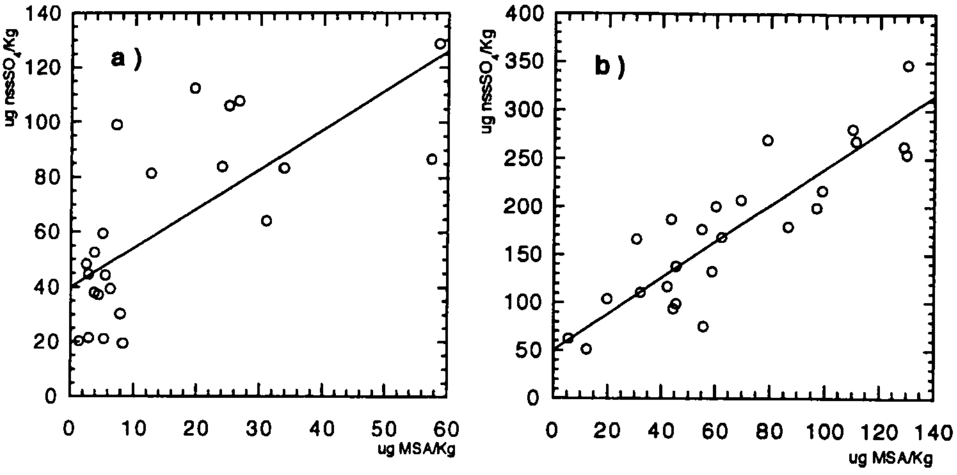

Figure 7 Plot of $nssSO_4$ concentration versus Na concentration; a) styx Glacier, b) Mc Carthy Ridge; ——— regression line.

The intercept is significant different from zero (95% probability level) and the slope is comparable with the mean values $nssSO_4$/MSA reported for ice cores and fresh snow from other coastal areas of Antarctica. For example, the following values are reported: 2.56 for an ice core of Law Dome east Antarctica[16], 2.5–10 for fresh summer snow of Dumont D'Urville[20] and 2.17–3.13 for ice cores of Antarctic peninsula[55]. For the Styx Glacier station, the linear association degree of $nssSO_4$ with MSA is much lower even though highly significant (99%). For this station, significant correlations were found also for NO_3 and nssCa, as reported in Table 3 in which, besides the correlation coefficients, the relative significant are indicated.

The variance of $nssSO_4$ is almost completely explained by the multiple regression model with MSA and NO_3 (Table 4a) or by the regression with MSA and nssCa (Table 4b). If all three variables (MSA, NO_3 and nssCa) are inserted in the regression model (Table 4c), no improvement is observed. A highly significant correlation between NO_3 and $nssSO_4$ is shown in Table 3, and the common variance between $nssSO_4$ and nssCa is already included in the model a, in Table 4. These considerations lead to conclude that in this station another source of $nssSO_4$ appears[56], in addition to that produced by DMS oxidation, which is correlated with NO_3 and/or with nssCa. A long range continental contribution of $nssSO_4$ has been recognised by Savoie *et al.*[57] at Mawson, from the relation between $nssSO_4$ and NO_3 and from the covariance of the latter with ^{210}Pb. This hypothesis can be extended also to the Styx Glacier station and an analogous behaviour is observed also with Mc Carthy Ridge samples (Table 4 d–f).

A confirmation of the different contributions to $nssSO_4$ in the two stations arises from the comparison of the mean $nssSO_4$/MSA ratio distributions: 3.27 (s = 2.00) for Mc Carthy Ridge, and 7.53 (s = 5.21) for Styx Glacier.

The increase of the $nssSO_4$/MSA ratio with altitude was reported also by Legrand and Saigne[57] comparing the values measured in ice cores sampled in both coastal and inland areas of Antacrtica. The values ranged from 2.27–5.26 for an ice core of D10, Terre Adelie[58] to values high as 10–33 measured on ice cores of the inland[59]. According to

Table 3 Correlation coefficients and significance levels in samples of Styx Glacier and Mc Carthy Ridge.

	$nssSO_4$	*MSA*	*NO_3*	*nssCa*
Styx Glacier				
$nssSO_4$	1.000	0.715	0.616	0.504
sig. level	–	0.000	0.002	0.017
MSA	0.715	1.000	0.083	0.168
sig. level	0.000	–	0.708	0.454
NO_3	0.616	0.083	1.000	0.601
sig. level	0.002	0.708	–	0.003
nssCa	0.504	0.168	0.601	1.000
sig. level	0.017	0.454	0.003	–
Mc Carthy Ridge				
$nssSO_4$	1.000	0.871	0.146	-0.102
sig. level	–	0.000	0.497	0.635
MSA	0.871	1.000	-0.181	-0.346
sig. level	0.000	–	0.398	0.098
NO_3	0.146	-0.181	1.000	0.351
sig. level	0.497	0.398	–	0.092
nssCa	-0.102	-0.346	0.351	1.000
sig. level	0.635	0.098	0.092	–

Shao-Meng LI *et al.*[60] the $nssSO_4$/MSA ratio increases with altitude also in the Arctic zone, with values ranging from 5.88 in Alert (Canada) to 16.67 in Dye3 (Greenland 2480 m a.s.l.) up to 20 at Summit (Greenland, 3200 m a.s..l).

Different hypotheses have been proposed to explain the variation of this ratio with altitude. Legrand[58] proposes a difference in origin of the air masses that transport $nssSO_4$ and MSA: for the coastal areas the air masses would origin by the closely ocean, whereas for the inland areas the air masses would came from the temperate zone. For these reasons the variation of the $nssSO_4$/MSA ratio depends upon the latitude at which the air masses originate. Other possible explanations involve: a) a different distribution of $nssSO_4$ and MSA in aerosols, with a subsequent modification of their deposition processes; b) different oxidation mechanisms of DMS with altitude; c) the existence of different contributions of $nssSO_4$ not originated by DMS oxidation.

As the two considered sampling stations are located at the same distance from the coast, the air masses active in both locations are presumably not different, and a different contribution of sulfates is responsible for the modified $nssSO_4$/MSA ratio[56].

Some unclarified aspects still exist in the cycle linking DMS, MSA and $nssSO_4$ albeit this cycle could have an important role in global climate changes as postulated by Charlson[61]. The use of MSA as an indicator of the biogenic source contribution is complicated by the variability, in space and time, of the $nssSO_4$/MSA ratios, that can be very different even in stations relatively close, as demonstrated in the Terra Nova Bay area.

Table 4 Multiple regression models in samples of Styx Glacier and Mc Carthy Ridge.

Styx Glacier

mod. a) $[nssSO_4] = 1.34[MSA] + 0.29[NO_3] + 14.6$

std. error	0.19	0.05	6.0
sig. level	0.000	0.000	0.025

$R^2 = 0.806$

mod. b) $[nssSO_4] = 1.26[MSA] + 0.75[nssCa] + 8.53$

std. error	0.26	0.26	12.1
sig. level	0.000	0.009	0.488

$R^2 = 0.626$

mod. c) $[nssSO_4] = 1.30[MSA] + 0.25[NO_3] + 0.17[nssCa] + 10.4$

std. error	0.20	0.06	0.24	9.03
sig. level	0.000	0.001	0.486	0.263

$R^2 = 0.791$

Mc Carthy Ridge

mod. d) $[nssSO_4] = 2.02[MSA] + 0.47[NO_3] + 9.53$

std. error	0.18	0.13	17.2
sig. level	0.000	0.001	0.585

$R^2 = 0.841$

mod. e) $[nssSO_4] = 2.06[MSA] + 1.30[nssCa] - 5.35$

std. error	0.22	0.59	29.7
sig. level	0.000	0.038	0.859

$R^2 = 0.786$

mod. f) $[nssSO_4] = 2.10[MSA] + 0.41[NO_3] + 0.79[nssCa] - 19.0$

std. error	0.19	0.13	0.52	25.3
sig. level	0.000	0.005	0.148	0.460

$R^2 = 0.850$

CONCLUSIONS

From the composition of snow samples collected in the area of Terra Nova Bay the different contributions of main elements may be individualized. Since the marine contribution changes with the climatic conditions, the E.F. obtained from mean concentrations, as usually reported, does not reveal the true effect of different sources.

The grouping samples on the basis of sea-salt content or seasonality exhibit a better information on the enrichment processes. Regression plots of different components versus sodium, considered an indicator of marine contribution, individualize quantitatively the non-sea-salt effect. So, while for Na, Cl and Mg only a marine contribution is observed, a constant excess of non sea spray K and Ca suggests the existence of a nearly uniform background aerosol over the investigated area.

The dominant source of $nssSO_4$ is the DMS oxidation but a very significant fraction is associated with NO_3 or nssCa. Significant correlations were found in the multiple variable regression analysis of $nssSO_4$, MSA, NO_3 and nssCa. The non-DMS fraction may be attributed to long range transport phenomena.

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